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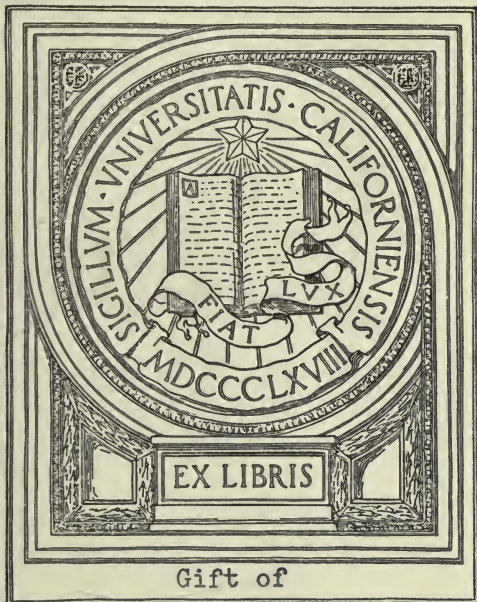
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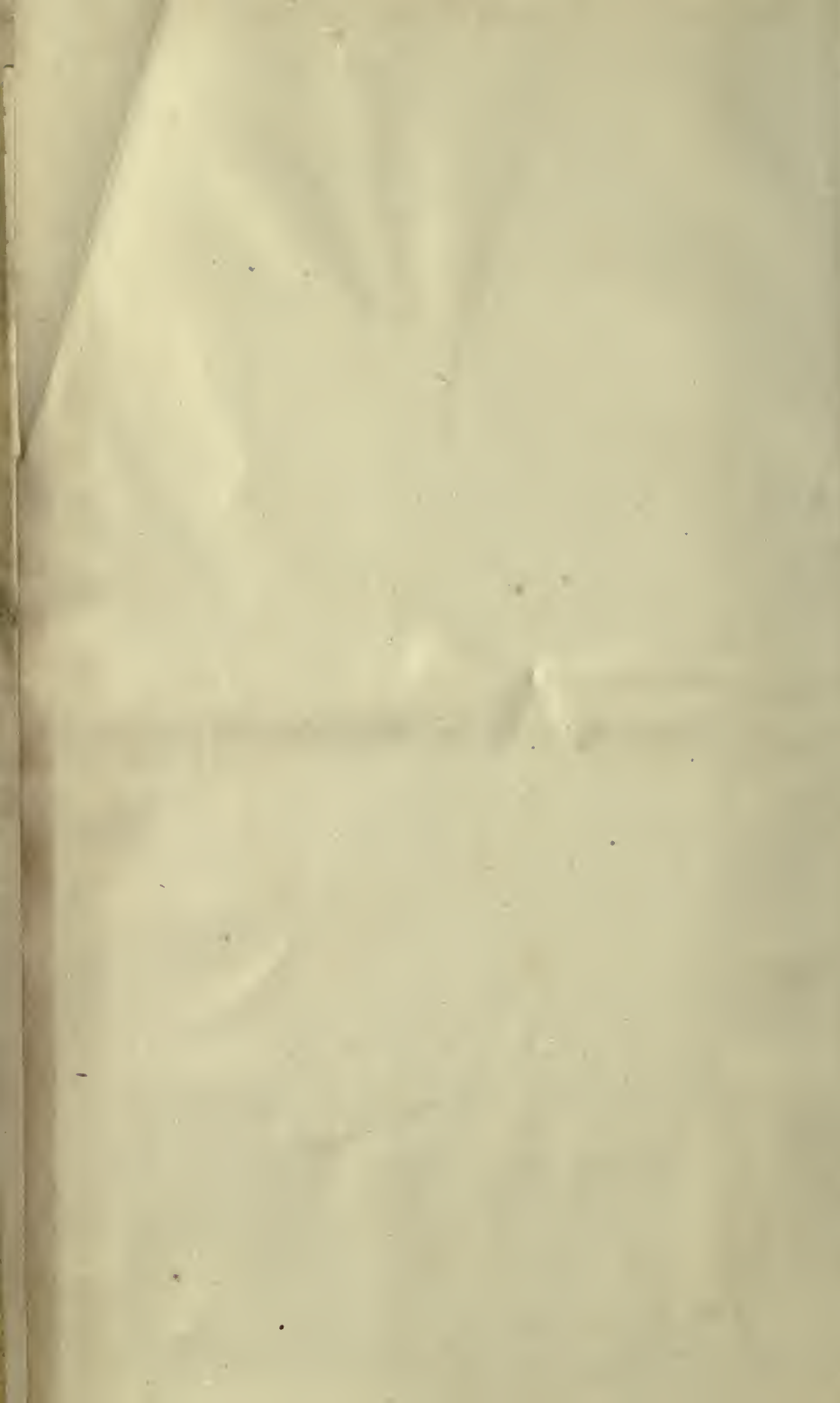
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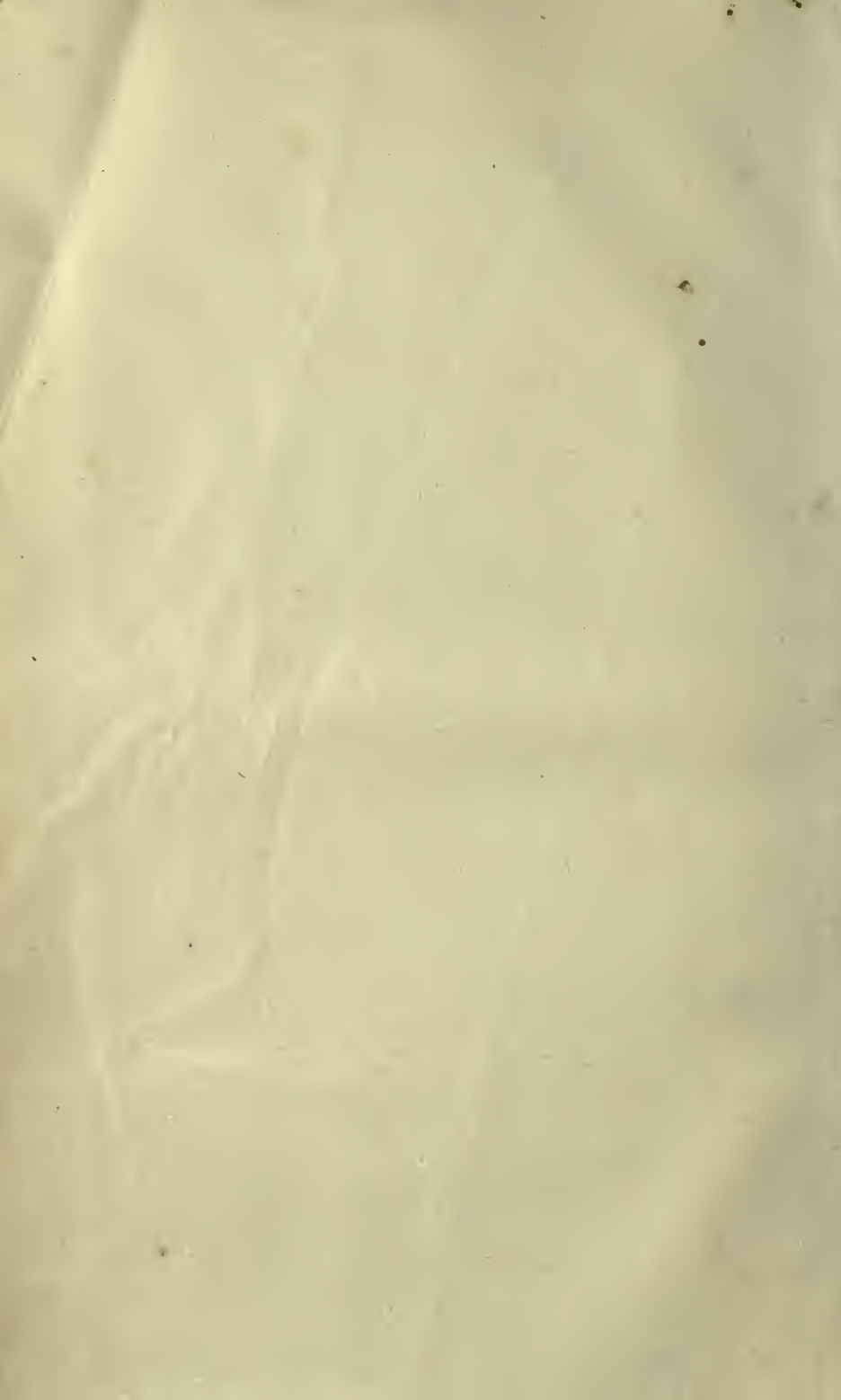
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ELEMENTS
OF
CHEMISTRY.

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**CHEMISTRY OF ORGANIC BODIES,
VEGETABLES,**

BY THOMAS THOMSON, M.D. F.R.S. L. & ED.

Regius Professor of Chemistry in the University of Glasgow, Corresponding
Member of the Royal Academy of Medicine of Paris.

One large vol. 8vo. of 1092 pages. London, 1838, in boards. £1 4s.

**AN OUTLINE OF THE
SCIENCES OF HEAT AND ELECTRICITY,**

BY THOMAS THOMSON, M.D. F.R.S. L. & ED.

Regius Professor of Chemistry in the University of Glasgow, Corresponding
Member of the Royal Academy of Medicine of Paris.

Second Edition, remodelled, and much enlarged. One vol. 8vo. illustrated with
Wood-cuts, 1840. 15s.

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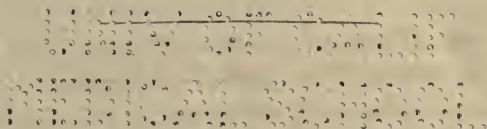
OF

CHEMISTRY,

INCLUDING THE APPLICATIONS OF THE SCIENCE IN
THE ARTS.

BY
THOMAS GRAHAM, F.R.S. L. & Ed.

PROFESSOR OF CHEMISTRY IN UNIVERSITY COLLEGE, LONDON; PRESIDENT
OF THE CHEMICAL SOCIETY; CORRESPONDING MEMBER OF THE ROYAL
ACADEMIES OF SCIENCES OF BERLIN AND MUNICH, &c.



LONDON:
HIPPOLYTE BAILLIERE,
Foreign Bookseller to the Royal College of Surgeons, and to the Royal Society,
219, REGENT STREET.

PARIS: J. B. BAILLIERE, RUE DE L'ECOLE DE MEDECINE.

LEIPZIG: T. O. WEIGEL,

1842.

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LONDON :

PRINTED BY SCHULZE AND CO. 13, POLAND STREET.

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P R E F A C E.

THE important bearings of the laws of heat, particularly in reference to the physical condition of matter, have led to their consideration before the chemical properties of substances, in this as in most other elementary treatises on chemistry. Light is then shortly considered, chiefly in reference to its chemical relations. The principles of its Nomenclature, in which compared with many sciences, chemistry has been highly fortunate, are then explained, together with the Symbolical Notation in use, by means of which the composition of highly compound bodies is expressed with the same palpable distinctness, which in arithmetic attends the use of figures, in place of words, for the expression of numerical sums.

A considerable section of the work is then devoted to the consideration of the fundamental doctrines of chemistry, under the heads of Combining Proportions, Atomic Theory, Doctrine of Volumes, Isomorphism, Isomerism, Constitution of Salts, and Chemical Affinity, including the propagation of this action through metallic and saline media, in the voltaic circle.

The materials of the Inorganic world are then described, under the two divisions of non-metallic elements and their compounds, and metallic elements and their compounds.

Lastly, the numerous compounds of the Organic world are discussed. In this department, a most extraordinary progress has been made within a very short period. The study of organic chemistry has also been much facilitated by classification,

and the arrangement under Compound Radicals, introduced by M. Liebig.

It was now obvious that the science was sufficiently advanced to be applied to the elucidation of the great questions of vegetable and animal physiology. A condensed view is given of the new discoveries in the former department, and also of the important conclusions respecting the animal functions of respiration and digestion, results which are entirely new, and now enter for the first time into a systematic work on Chemistry.

University College,
November, 1841.

ERRATA.

- Page 22, line 18, *for* iron melts *read* cast iron melts
- .. 55, in table *for* temperature 242° *read* 212°
- .. 59, in figure 3, introduce *d* in the upper circle, and *f* in the lower square
- .. 61, in the figure, the tubes should be represented not open, but closed at the top
- .. 120, second line from bottom *for* 1895.5 *read* 1894.5
- .. 121, lines 18 and 19, *for* 1294.5 and 1795.5 *read* 1394.5 and 1895.5
- .. 130, in the diagram representing the combining measure of chlorine *for* 1269.5 inscribed in each square *inscribe* 2470
- .. 134, 9 lines from bottom *for* chloroform *read* chloroform
- .. 149, line 13, *for* Fe_2O_3 *read* FeO, SO_3
- .. 155, line 16, *for* similarity of form *read* similarity of composition
- .. 177, line 21, *for* Ag *read* Hg
- .. 202, in figure 4, transpose the terms austral pole and boreal pole
- .. 210, in figure 12, *insert* E at the top and A at the bottom of the semicircle
- .. 290, line 7 from bottom, *for* 1039×34 , *read* 1039.3×4
- .. 296, line 6, *for* best soluble *read* least soluble
- .. 312, line 13, *for* SiO_3 , *read* Si
- .. 314, line 16, *dele* be
- .. 322, to table of sulphurous acid series, add :
- Crystals of the leaden chambers (de la Provostaye) $\text{SO}_2 + \text{Cl} + \text{SO}_2\text{O}$
- Oxichloride of sulphur (H. Rose) $\text{SO}_2 + \text{Cl} + \text{SO}_2\text{O}$
- .. 330, line 10 from bottom, *for* Herschell *read* Herschel
- .. 336, line 15, *for* hyposulphite *read* hyposulphate
- .. 362, in table of chlorides, *for* hypochlorus *read* hypochlorous
- .. 390, line 8, *for* iodate *read* iodite
- .. 405, line 12 from bottom, *for* seleniuretted *read* seleniatted
- .. 424, line 17 from bottom, *for* half *read* twice
- .. 468, line 6, *for* 11 times *read* $5\frac{1}{2}$ times
- .. 471, line 8, *for* 12,000 tons *read* 40,000 tons
- .. 478, line 18, after not efflorescent *dele* when free from carbonate, and *insert* although injured by acid fumes
- .. 596, line 1, *for* Pattenson *read* Pattinson
- .. 618, line 1, *for* $\text{Na} + \text{O}_2\text{WO}_2$ *read* $\text{NaO} + 2\text{WO}_2$
- .. 652, line 13, *for* chloride of strontium *read* bromide of strontium
- .. 684, line 13, *for* hydrochlorate *read* chloride
- .. 927, line 9 from bottom, *for* vegetables *read* nutgalls

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ELEMENTS

OF

CHEMISTRY.

CHAPTER I.

HEAT.

THE objects of the material world are altered in their properties by heat in a very remarkable manner. The conversion of ice into water, and of water into vapour, by the application of heat, affords a familiar illustration of the effect of this agent in changing the condition of bodies. All other material substances are equally under its influence; and it gives rise to numerous and varied phenomena, demanding the attention of the chemical inquirer.

Heat is very readily communicated from one body to another; so that when hot and cold bodies are placed near each other, they speedily attain the same temperature. The obvious transference of heat in such circumstances impresses the idea that it possesses a substantial existence, and is not merely a quality of bodies, like colour or weight; and when thus considered as a material substance, it has received the name *caloric*. It would be injudicious, however, to enter at present into any speculation on the nature of heat; it is sufficient to remark that it differs from matter as usually conceived, in several respects. Our knowledge of heat is limited to the different effects which it produces upon bodies, and the mode of its transmission; and these subjects may be considered without reference to any theory of the nature of this agent.

The subject of heat will be treated of under the following heads :

1. Expansion, the most general effect of heat, and the Thermometer.
2. Specific Heat.
3. The communication of heat by Conduction and Radiation.
4. Liquefaction, as an effect of heat.
5. Vaporization, or the gaseous state, as an effect of heat.
6. Speculative notions which have been entertained respecting the Nature of heat.

EXPANSION AND THE THERMOMETER.

All bodies in nature, solids, liquids, or gases, suffer a temporary increase of dimension when heated, and contract again into their original volume on cooling.

1. *Expansion of solids.* The expansion of solid bodies, such as the metals, is by no means considerable, but may readily be made sensible. A bar of iron, which fits easily when cold into a gauge, will be found, on heating it to redness, to have increased sensibly both in length and thickness. The expansion and contraction of metals, indeed, and the immense force with which these changes take place, are matters of familiar observation, and are often made available in the arts. The iron hoops of carriage wheels, for instance, are applied to the frame while they are red hot, and in a state of expansion, and being then suddenly cooled by dashing water upon them, they contract and bind the wood work of the wheel with great force. The expansion of solids, however, is very small, and requires nice measurement to ascertain its amount. The expansion in length only has generally been determined, but it must always be remembered that the body expands also in its other dimensions, in an equal proportion. The first general fact observable is, that the amount of dilatation by heat is different in different bodies. No two solids expand alike. The metals expand most, and their rates of expansion are best known. Rods of the undermentioned substances, on being heated from the freezing to the boiling point of water, elongate as follows :

Lead	.	.	.	1	on	351	Pure Gold	.	1	on	632
Silver	.	.	.	1	„	524	Iron Wire	.	1	„	812
Copper	.	.	.	1	„	581	Platinum	.	1	„	1167
Brass	.	.	.	1	„	584	Flint Glass	.	1	„	1248

This is the increase which these bodies sustain in length. Their increase in general bulk is about three times greater. Thus, if glass elongates 1 part in 1248 from the freezing to the boiling point of water, it will dilate in cubic-capacity 3 parts in 1248 or 1 part in 416. The expanded bodies return to their original dimensions on cooling. Wood does not expand much in length; hence it is occasionally used as a pendulum rod. For the same reason a slip of marble has lately been employed for that purpose, in constructing the clock of the Royal Society of Edinburgh. Flint glass expands by the table $\frac{1}{1748}$ th part, while the metal platinum expands very little more, ($\frac{1}{1167}$). Hence the possibility of cementing glass and platinum together, as is done in many chemical instruments. Other metals pushed through the glass when it is red hot and soft, shrink afterwards so much more than the glass on cooling, as to separate from it, and become loose. Lead is the most expansible of the metals; it expands between three and four times more than platinum from the same heat.

By far the most important discovery in a theoretical point of view, that has been made on the subject of the dilatation of solids by heat, is the observation of Professor Mitscherlich of Berlin, that the angles of some crystals are affected by changes of temperature. This proves that some solids in the crystalline form do not expand uniformly, but more in one direction than in another. Indeed, Mitscherlich has shewn that while a crystal is expanding in length by heat, it may actually be contracting at the same time in another dimension. An angle of rhomboidal calcareous spar alters eight and a half minutes of a degree between the freezing and boiling points of water. But this unequal expansion does not occur in crystals of which all the sides and angles are alike, as the cube, the regular octohedron, the rhomboidal dodekahedron. In investigating the laws of expansion among solids, it is adviseable, therefore, to make choice of crystallized bodies. For, in a substance not regularly crystallized, the expansion of different specimens may not be precisely the same, as the internal structure may be different. Hence the expansions of the same substance, as given by different experimenters, do not always exactly correspond. The same glass has been observed to dilate more when in the form of a solid rod, than in that of a

tube ; and the numerous experiments on uncrystallized bodies, which we possess have afforded no ground for general deductions.

It has been farther observed, that the same solid is more expansible at high than at low temperatures, although the increase in the rate of expansion is in general not considerable. Thus, if we mark the progress of the dilatation of a bar of iron under a graduated heat, we find that the increase in dimension is greater for one degree of heat near the boiling point of water than for one degree near its freezing point. Solids are observed to expand at an accelerated rate, in particular, when heated up to near their fusing points. The cohesion or attraction which subsists between the particles of a solid is supposed to resist the expansive power of heat. But many solids become less tenacious, or soften before melting, which may account for their increasing expansibility. Platinum is the most uniform in its expansions of the metals.

Such changes in bulk, from variations in temperature, take place with irresistible force. This was well illustrated in an experiment, which was successfully made upon a gallery in the Museum of Arts and Manufactures in Paris, in order to preserve it. The opposite walls of this edifice were bulging outwards, from the pressure of the floors and roof, which endangered its stability. By the directions of an ingenious mechanic, stout iron rods were laid across the building, with their extremities projecting through the opposite walls. The rods were then strongly heated by a number of lamps, and when in an expanded condition, a disc on either extremity of each rod was screwed firmly up against the external surface of the wall. On afterwards allowing the rods to cool, they contracted, and drew the walls to which they were attached somewhat nearer together. The process was several times repeated, till the walls were restored to a perpendicular position.

The force of expansion always requires to be attended to in the arts, when iron is combined in any structure with less expansible materials. The cope-stones of walls are sometimes held together with clamps, or bars of iron : such bars, if of cast iron, which is brittle, often break on the first frost, from a tendency to contract more than the stone will permit ; if of malleable iron, they generally crush the stone, and loosen them-

selves in their sockets. When cast iron pipes are employed to conduct hot air or steam through a factory, they are never allowed to abut against a wall or obstacle which they might in expanding overturn.

A compound bar, made by soldering together two thin plates of copper and platinum, affords a good illustration of unequal expansion by heat. The copper plate, being much more expandible than platinum, the bar is bent upon the application of heat to it; and in such a manner, that the copper is on the outside of the curve. It may easily be conceived, that by a proper attention to the expansions of the metals of which it is composed, a bar of this kind might be so constructed, that although it was heated and expanded, its extreme points should always remain at the same distance from each other, the lengthening being compensated for by the bending. The balance wheels of chronometers are preserved invariable in their diameters, at all temperatures, by a contrivance of this kind. It has also been applied to the construction of a thermometer of solid materials—that of Breguet.

When hot water is suddenly poured upon a thick plate of glass, the upper surface is heated and expanded before the heat penetrates to the lower surface of the plate. There is here unequal expansion, as in the case of the slip of copper and platinum. The glass tends to bend, with the hot and expanded surface on the outside of the curve, but is broken from its want of flexibility. The occurrence of such fractures is best avoided by applying heat to glass vessels in a gradual manner, so as to occasion no great inequality of expansion; or by using very thin vessels, through the substance of which heat is rapidly transmitted.

This effect of heat on glass may by a little address be turned to advantage. Watch glasses are cut out of a thin globe of glass, by conducting a crack in a proper direction, by means of an iron rod, or piece of tobacco pipe, heated to redness. Glass vessels damaged in the laboratory may often be divided in the same manner, and still made available for many useful purposes.

Both cast iron and glass are peculiarly liable to accidents from unequal expansion, when in the state of flat plates. Plate glass indeed can never be heated without risk of its breaking. The flat iron plates placed across chimneys as dampers, are also

very apt to split when they become hot, and much inconvenience has often been experienced in manufactories from this cause. A slight curvature in their form has been found to protect them most effectually.

Expansion of liquids. In liquids the expansive force of heat is little resisted by cohesive attraction, and is much more considerable than in solids. This fact is strikingly exhibited by filling the bulb and part of the stem of a common thermometer tube with a liquid, and applying heat to it. The liquid is seen immediately to mount in the tube.

The first law in the case of liquids is that some expand much more considerably by heat than others. Thus, on being heated to the same extent, namely, from the freezing to the boiling point of water,

Spirits of wine expand	$\frac{1}{9}$	that is,	9 measures become	10
Fixed oils	$\frac{1}{12}$	„	12	„ 13
Water	$\frac{1}{22.76}$	„	22.76	„ 23.76
Mercury	$\frac{1}{55.5}$	„	55.5	„ 56.5

Spirits of wine are, therefore, six times more expansible by heat than mercury is. The difference in the heat of the seasons affects sensibly the bulk of spirits. In the height of summer spirits will measure 5 per cent more than in the depth of winter.

The new liquids produced by the condensation of gases appear to be characterized by an extraordinary dilatability. M. Thilorier has observed that fluid carbonic acid is more expansible by heat than air itself; heated from 32° to 86°, twenty volumes of this liquid increase to twenty-nine, which is a dilatation four times greater than is produced in air, by the same change of temperature.* Mr. Kemp has extended this observation to liquid sulphurous acid and cyanogen, which although not possessing the excessive dilatability of liquid carbonic acid, are still greatly more expansible than ordinary liquids. Sir D. Brewster had several years before discovered certain fluids in the minute cavities of topaz and quartz, which seemed to bear no analogy to any other known liquid in their extraordinary dilatability. They do not appear to have been entirely liquefied gases, but probably were so in part.†

* Annales de Chimie et de Physique, t. 60, p. 427.

† Edinburgh Phil. Trans. vol. x. 1824.

A singular correspondence has been observed, by M. Gay-Lussac, between two particular liquids—alcohol and sulphuret of carbon, in the amount of their expansion by heat; although each of these liquids has a particular temperature at which it boils—

Alcohol at 173°

Sulphuret of carbon at 116°

still the ratios of expansion from the addition, and of contraction from the loss of heat, are found to be uniformly the same in the case of these two liquids, which are the only ones known to possess such a relation. The number of liquids, however, the expansions of which, under different degrees of heat, have been examined, is exceedingly small; although comparative experiments may be made with much greater facility in regard to liquids than solids.

The second law is, that liquids are progressively more expandible at higher than at lower temperatures. This is less the case with mercury, perhaps, than with any other liquid. The expansions of that liquid are, indeed, so uniform, as to render it extremely proper for the construction of the thermometer, as will afterwards appear. The rate of expansion of mercury was determined with extraordinary care by Dulong and Petit.

From 1° to 100° centigrade, mercury expands 1 measure on $55\frac{1}{2}$

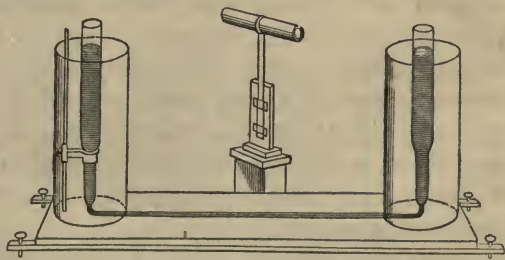
„ 100° „ 200° „ „ „ 1 „ $54\frac{1}{4}$

„ 200° „ 300° „ „ „ 1 „ 53

According to the same experimenters, the expansion of mercury, confined in glass tubes, is only 1 on 64.8. The dilatation of the glass causes the capacity of the instrument to be enlarged, so that the whole expansion of the mercury is not indicated. The only mode in which the error introduced by the expansion of the enclosing

vessel can be avoided, in ascertaining the expansions of liquids, is that practised by Dulong and Petit; namely, heating

the liquid in one limb of a syphon, (see Figure) and observing how high it rises above the level of the same liquid in the other



limb, kept at a constant temperature. The columns of course balance each other, and the shorter column of dense fluid supports a longer column of dilated fluid. All other modes of obtaining the absolute expansions of liquids are fallacious.

No progress has yet been made in discovering the law by which expansions of liquids are regulated; for the complicated mathematical formulæ of Biot, Dr. Young, and others, are mere general expressions for these expansions, which proceed upon no ascertained physical principle. Some theory must be formed of the constitution of liquids, before we can hope to account for their expansions.

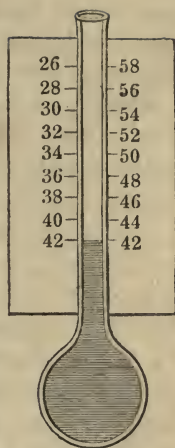
Count Rumford ascertained the contraction of water for every $22\frac{1}{3}^{\circ}$, in cooling from 212° to 32° . The results were as follows, 2000 measures of water contract—

In cooling $22\frac{1}{2}^{\circ}$, or from 212° to	$189\frac{1}{2}$.	18	measures.
„ „	$189\frac{1}{2}$	„	167	. 16.2 „
„ „	167	„	$144\frac{1}{2}$. 13.8 „
„ „	$144\frac{1}{2}$	„	122	. 11.5 „
„ „	122	„	$99\frac{1}{2}$. 9.3 „
„ „	$99\frac{1}{2}$	„	77	. 7.1 „
„ „	77	„	$54\frac{1}{2}$. 3.9 „
„ „	$54\frac{1}{2}$	„	32	. 0.2 „

The expansion of water, by heat, is subject to a remarkable peculiarity which occasions it to be extremely irregular, and demands special notice. This liquid, in a certain range of temperature, becomes an exception to the very general law that bodies expand by heat. When heat is applied to ice-cold water, or water at the temperature of 32° , this liquid, instead of expanding, contracts by every addition of heat, till its temperature rises to 40° at, or very near which temperature water is as dense as it can be. And, conversely, when water of the temperature of 40° is exposed to cold, it actually expands with the progress of the refrigeration. Water may, with caution, be cooled 20 or 25 degrees below its freezing point, in the fluid form, and still continue to expand. It is curious that this liquid, in a glass bulb, expands as nearly as possible to the same amount, on each side of 42° when either heated or cooled the same number of degrees. Hence when cooled to 40° it rises to the same point in the stem as when heated to 44° ; at 32° it stands at the same point as at 52° , and so on for different temperatures, as illustrated in the graduation of the figure. The expansion of water by cold, under

40° is certainly not very great, being little more than 1 part in 1000 at 32°; hence it was early suspected that it might be an illusion, from the contraction of the glass bulb (in which the experiment was always made) forcing up the water in the stem. But all grounds of objection on this score have been removed by the mode in which the experiment has subsequently been conducted, particularly in the admirable researches of Dr. Hope on this subject.

Dr. Hope carried a deep glass jar, filled with water of the temperature 50°, into a very cold room; and having immersed two small thermometers in the water, one near the surface, and the other at the bottom of the jar, watched their indications as the cooling proceeded. The thermometer above indicated a temperature higher by several degrees than the thermometer below, till the temperature fell to 40°, that is, the chilled water fell as usual to the bottom of the jar, or became denser as it lost heat, as illustrated in Figure 1. At 40° the two thermometers were for some time steady, (Fig. 2.) but as the cooling proceeded



beyond that point, the instrument in the higher situation indicated the lower temperature (Fig. 3); or the water now as it became colder, became lighter, and rose to the top. A better demonstration of the fact in question could not be devised.

FIG. 1.
In cooling
above 40°.



FIG. 2.



FIG. 3.
In cooling
below 40°.



Great pains have been taken by several philosophers to determine the exact temperature of this turning point, at which water possesses its maximum density. By the recent elaborate experiment of Hållstrom, this point is 39°.38. Sir C. Blagden and Mr. Gilpin had made it 39°. Dr. Hope had estimated it at 39½°.

When salt is dissolved in water, the temperature of the maximum density becomes lower and lower, in proportion to the quantity of salt in solution, and sinking below the freezing

point of the liquid, the anomaly disappears. This is the reason why the interesting fact we have been discussing cannot be observed in the case of sea water.

There is a solid body which presents the only other known parallel case of progressive contraction by heat; this is Rose's fusible metal, which is an alloy of

2 parts by weight of Bismuth

1 part „ „ „ „ Lead

1 „ „ „ „ „ Tin.

A bar of this metal expands progressively, like other bodies, till it attains the temperature of 111° ; it then rapidly contracts by the continued addition of heat, and at 156° attains its maximum density, occupying less space than it does at the freezing point of water. It afterwards progressively expands melting at 201° . It may be remarked, however, of this body, that it is a chemical compound, of a kind in which a change of constitution is very likely to occur from a change in temperature; and that it cannot, therefore, be fairly compared with water.

The dilatation which water undergoes below 40° has been supposed to be connected with its sudden increase of volume in freezing, for ice is specifically lighter than water, in the proportion of 92 to 100. The water, it is said, may begin to pass partially into the solid form at 40° , although the change is not complete till the temperature sinks to 32° . But such an assumption is altogether gratuitous, and improbable in the extreme.

The extraordinary irregularity in the dilatation of water by heat is not only curious in itself, but also of the utmost consequence in the economy of nature. When the cold season sets in, the surface of our rivers and lakes is cooled by the contact of the cold air and other causes. The superficial water so cooled, sinks and gives place to warmer water from below, which, chilled in its turn, sinks in like manner. The progress of cooling in the lake goes on with considerable rapidity, so long as the cold water descends and exposes that not hitherto cooled. But this *circulation*, which accelerates the cooling of a mass of water in so extraordinary a degree, ceases entirely when the whole water has been cooled down to the temperature of 40° , which is still 8 degrees above the freezing point. Thereafter the chilled surface water expands as it loses its heat, and remains on the top, from its lightness, while the cold is very

imperfectly propagated downwards. The surface in the end freezes, and the ice may thicken, but at the depth of a few feet, the temperature is not under 40° , which is high when compared with that frequently experienced, even in this climate, during winter.

If water continued to become heavier, until it arrived at the freezing temperature, the whole of it would be cooled to that point before ice began to be formed; and the consequence would be, that the whole body of water would rapidly be converted into ice, to the destruction of every being that inhabits it. Our warmest summers would make but little impression upon such masses of ice; and the cheerful climate, which we at present enjoy, would be less comfortable than the frozen regions of the pole. Upon such delicate and beautiful adjustments, do the order and harmony of the universe depend.

Expansion of Gases. The expansion by heat in the different forms of matter is exceedingly various.

By being heated from 32° to 212° ,

1000 cubic inches of iron become 1004.

1000 „ water „ 1045.

1000 „ air „ 1375.

Gases are, therefore, more expansible by heat than matter in the other two conditions of liquid and solid. The reason is, that the particles of air or gas, far from being under the influence of cohesive attraction, like solids or liquids, are actuated by a powerful repulsion for each other. The addition of heat mightily enhances this repulsive tendency, and causes great dilatation.

The rate of the expansion of air and gases from increase of temperature, was involved in considerable uncertainty till a recent period. This arose from the neglect of the early experimenters to *dry* the air or gas upon which they operated. The presence of a little water by rising in the state of steam into the gas, on the application of heat, occasioned great and irregular expansions. But in 1801, the law of the dilatation of gases was discovered by M. Guy-Lussac, of Paris, and by our countryman, Dr. Dalton, independently of each other. By keeping the gases experimented upon dry, these philosophers were enabled to discover that *all gases* experience the same increase in volume by the application of the same degree of heat.

Dr. Dalton confined a small portion of dry air over mercury in a graduated tube. He marked the quantity by the scale, and the temperature by the thermometer. He then placed the whole in circumstances where it was uniformly heated up to a certain temperature, and observed the expansion. Guy-Lussac's apparatus was more complicated, but calculated to give very precise results. He found that 1000 volumes of air, on being heated from 32° to 212° , become 1375, which agreed very closely with the result of Dr. Dalton. Mr. James Crichton, of Glasgow, has lately confirmed this determination, finding that 1000 volumes of air become 1374.8.

It follows consequently that air at the freezing point expands $\frac{1}{480}$ th part of its bulk for every added degree of heat on Fahrenheit's scale : that is—

480 cubic inches at 32° become	
481 ,, 33°	
482 ,, 34° &c.	

increasing one cubic inch for every degree. A contraction of one cubic inch occurs for every degree below 32° .

480 cubic inches at 32° become	
479 ,, 31°	
478 ,, 30°	
477 ,, 29° &c.	

We can easily deduce, from this law, the expansion which a certain volume of gas at a given temperature will undergo, by heating it up to any particular temperature; or the contraction that will result from cooling. Air, of the temperature of freezing water, has its volume doubled when heated 480 degrees, and when heated 960 degrees, or twice as intensely, its volume is trebled, which is the effect of a low red heat.

Hydrogen gas, steam, and the vapour of sulphuric ether were found to expand in the same proportion as air. It has hence been concluded that the rate of expansion is the same in all gaseous fluids. It is to be observed also, that in the same air or gas, the rate of expansion continues uniform at all temperatures.

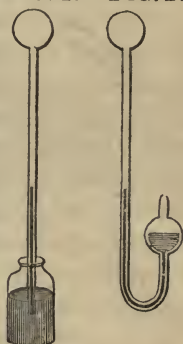
THE THERMOMETER.

An instrument for indicating variations in the intensity of heat, or degrees of temperature, by their effect in expanding some body, was invented more than two centuries ago, and has received successive improvements.

The expansions of solids are too minute to be easily measured, and cannot, therefore, be conveniently applied to mark degrees of heat. Air and gases, on the other hand, are so much dilated by a slight increase of heat, that they are not calculated for ordinary purposes. The first thermometer constructed, however, that of Sanctorio, was an air one. FIG. 1. FIG. 2. A glass tube, open at one end, with a bulb blown upon the other, (Fig. 1.) was slightly heated, so as to expel a portion of the air from it, and then the open end of the tube was dipped under the surface of a coloured fluid, which was allowed to rise into the tube, as the air cooled and contracted. When heat, the heat of the hand for instance, is applied to the bulb, the air in it is expanded, and depresses the column of coloured fluid in the tube. A useful modification of the air thermometer, for researches of great delicacy, was contrived by Sir John Leslie, under the name of the Differential thermometer. In this instrument, two close bulbs are connected by a syphon containing a coloured liquid, (Fig. 2.) If both bulbs be equally heated, the air in each is equally expanded, and the liquid between them remains stationary. But if the upper bulb only be heated, then the air in that bulb is expanded, and the column of liquid depressed. It is, therefore, the difference of temperature between the two bulbs which is indicated.

But liquids fortunately are intermediate in their expansions between solids and gases, and when contained in a glass vessel of a proper form, the changes of bulk which they undergo can be indicated to any degree of precision.

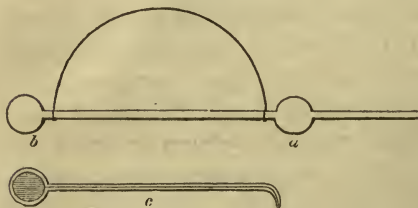
A hollow glass stem or tube is selected, the calibre or bore of which may be of any convenient size, but must be uniform, or



not wider at one place than another. Tubes of very narrow bore, and which are called *capillary*, the bore being like a hair in magnitude, are now alone employed. Such tubes are made by rapidly drawing out a hollow mass of glass while soft and ductile under the influence of heat. The central cavity still continues, becoming the bore of the tube, and would not cease to exist although the tube were drawn out into the finest thread. From the mode in which capillary tubes are made, their equality of bore and suitableness for thermometers, cannot always be depended upon. The bore is frequently conical, or wider at one end than at the other. It is tested by drawing up into the tube a little mercury, as much as fills a few lines of the cavity. The little column is then moved progressively along the tube, and its length accurately measured, at every stage, by a pair of compasses. The column will measure the same in every part of the tube, provided the bore does not alter. Not more than one-sixth part of the tubes made are found to possess this requisite.

Satisfied with the regularity of the bore, the thermometer-maker softens one extremity of the tube, and blows a ball upon it. This is not done by the mouth, which would moisten the interior, by introducing watery vapour, but by means of an elastic bag of caoutchouc, which is fitted to the open end of the tube. He then marks off the length which the thermometer ought to have, and above that point expands the tube into a second bulb a little larger than the first. It has then the form of Figure 3. After cooling, the open extremity of the tube is

FIG. 3.



plunged into distilled and well-boiled mercury, and one of the bulbs heated so as to expel air from it. During the cooling, the mercury is drawn up and rises into the ball *a*. It is made

to pass from thence into the ball *b*, by turning the instrument, so that *b* is undermost, and then expelling the air from that bulb by applying heat to it, after which the mercury descends from the effect of cooling. The ball *b*, being entirely filled with mercury, and a portion left in *a*, the tube is supported by an iron wire, as represented in the figure, over a charcoal fire,

where it is heated throughout its whole length, so as to boil the mercury, the vapour of which drives out all the air and humidity, and the balls contain at the end nothing but the metal and its vapour. The open end of the tube, which must not be too hot, is then touched with sealing wax, which is drawn into the tube on melting, and solidifies there on protecting that end of the tube from the heat. That being done, the thermometer is immediately withdrawn from the fire, and being held with the end sealed with wax uppermost, during the cooling the ball *b*, and the portion of the tube below the ball *a*, are filled with mercury. After cooling, the instrument is inclined a little, and by warming the lower ball, a portion of mercury is expelled from it, so that the mercury may afterwards stand at a proper height in the tube when the instrument is cold. The tube is then melted with care by the blow-pipe flame below the ball *a*, and closed, or hermetically sealed, as in *c*. The thermometer is in this way properly filled with mercury, and contains no air.

We have now an instrument in which we can nicely measure and compare any change in the bulk of the included fluid metal. Having previously made sure of the equality of the bore, it is evident that if the mercury swells up and rises two, three, four, or five inches in the tube, it has expanded twice, thrice, four or five times more than if it had risen only one inch in the tube. By placing a graduated scale against the tube, we can, therefore, learn the quantity of expansion by simple inspection.

In order to have a fixed point on the scale, from which to begin counting the expansion of mercury by heat, we plunge the bulb of the thermometer into melting ice, and put a mark on the stem at the point to which the mercury falls. However frequently we do so with the same instrument, we shall find that the mercury always falls to the same point. This is, therefore, a fixed starting point. We obtain another fixed point by plunging the thermometer into boiling water. With certain precautions, this point will be found equally fixed on every repetition of the experiment. The most important of these precautions is, that the barometer be observed to stand at 29.8 inches, when the boiling point is taken. It will afterwards be explained that the boiling point of water varies with the atmospheric pressure to which it is subject at the time.

Thermometers which are properly closed, and contain no air,

can be inverted without injury, and the mercury falls into the tube, producing a sound as water does in the water-hammer. When the instrument contains air, the thread of mercury is apt to divide on inversion, or from other circumstances. When this accident occurs, it is best remedied by attaching a string to the upper end of the instrument, and whirling it round the head. The detached little column of mercury generally acquires in this way a centrifugal force, which enables it to pass the air, and rejoin the mercury in the bulb.

When the glass of the bulb is thin, it is proper to seal the tube as described, and to retain it for a few weeks before marking upon it the fixed points. Thermometers, however carefully graduated at first, are found in a short time to stand above the mark in melting ice, unless this precaution be attended to. Old instruments often err by as much as half a degree, or even a degree and a half in this way. The effect is supposed to arise from the pressure of the atmosphere upon the bulb, which, when not truly spherical, seems to yield slightly, and in a gradual manner. The chance of this defect may be avoided by giving the bulb a certain thickness. Mr. Crichton's thermometers, of which the freezing point has not altered in forty years, were all made unusually thick in the glass. But this thickness has the disadvantage of diminishing the sensibility of the instrument to the impression of heat.

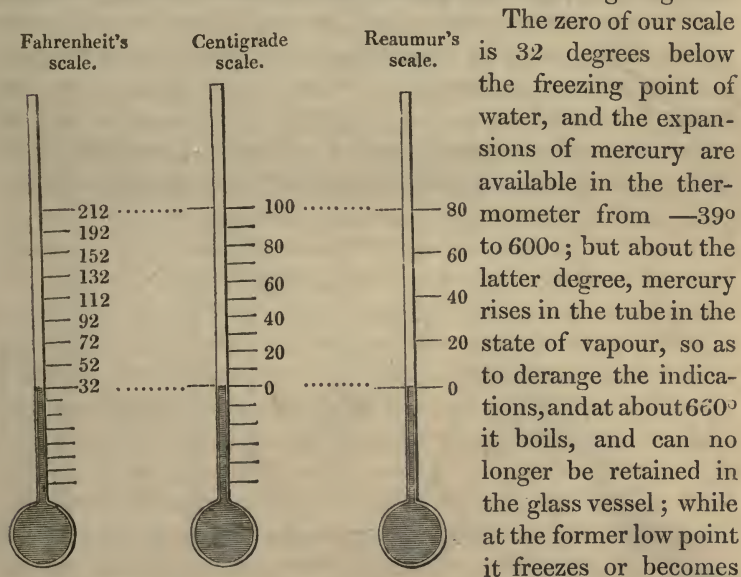
We have in this way the expansion marked off on the tube, which takes place between the freezing and boiling points of water. On the thermometer which is used in this country, and called Fahrenheit's, this space is subdivided into 180 equal parts, which are called degrees. This division appears empirical, and different reasons are given why it was originally adopted. Fahrenheit was an instrument-maker in Hamburgh, and as he kept his process for graduating thermometers a secret, we can only form conjectures as to what were the principles that guided him.

It is more convenient to divide the space between the freezing and boiling of water into 100 equal parts, which was done in the instrument of Celcius, a Swedish philosopher. This division was adopted at a later period in France, under the designation of the centigrade scale, and is now generally used over the continent. The freezing point of water is called C, or zero, and the boiling point 100. But in our scale, the

point is arbitrarily called 32° , or the 32nd degree; and consequently the boiling point is 32 added 180, or the 212th degree.*

The scale can easily be prolonged to any extent, above or below these points, by marking off equal lengths of the tube for 180 degrees, either above or below the space first marked. The degrees of contraction below zero, or 0° , are marked by the minus sign (—), and called negative degrees, in order to distinguish them from degrees of the same name above zero, or positive degrees. Thus, 47° means the 47th degree above zero, — 47° , the 47th degree under zero.

The only other scale in use is that of Reaumur, in the north of Germany. The expansion between the freezing and boiling of water is divided into 80 parts in this thermometer. The relation between the three scales is illustrated in the following diagram.



The zero of our scale is 32 degrees below the freezing point of water, and the expansions of mercury are available in the thermometer from -39° to 600° ; but about the latter degree, mercury rises in the tube in the state of vapour, so as to derange the indications, and at about 660° it boils, and can no longer be retained in the glass vessel; while at the former low point it freezes or becomes

* A simple rule may be given for converting centigrade degrees into degrees Fahrenheit. 100 degrees Centigrade being equal to 180 degrees Fahrenheit, 10 degrees C. = 18 degrees F., or 5 degrees C. = 9 degrees F.; multiply the Centigrade degrees by 9, and divide by 5, and add 32. Thus to find the degree F. corresponding with 50° C.

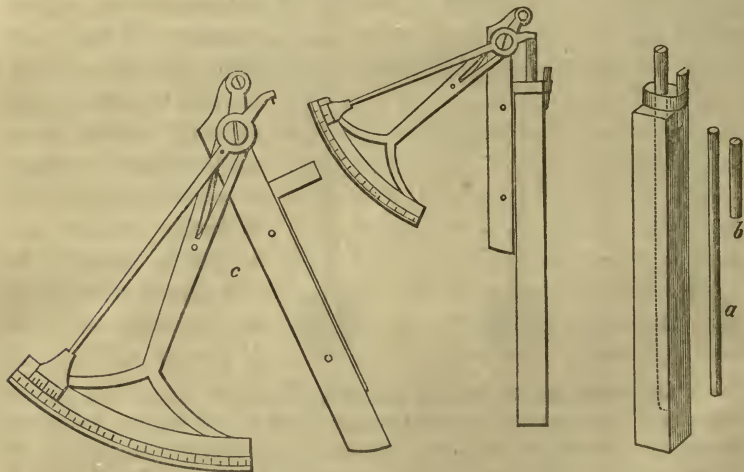
$$\begin{array}{r} 50 \\ 9 \\ \hline 5)450 \\ 90 \\ \hline \text{add } 32 \end{array}$$

Or the 50° C. corresponds with the 122° F.

solid. For degrees of cold below the freezing point of mercury, we must be guided by the contractions of alcohol, or spirits of wine, a liquid which has not been frozen by any degree of cold we are capable of producing. There is no reason, however, for believing that we have ever descended more than 130 or 140 degrees below our zero.

The zero of these scales has, therefore, no relation to the *real zero* of heat, or point at which bodies have lost all heat. Of this point we know nothing, and there is no reason to suppose that we have ever approached it. The scale of temperature may be compared to a chain, extended both upwards and downwards beyond our sight. We fix upon a particular link, and count upwards and downwards from that link, and not from the beginning of the chain.

The means of producing heat are much more at our command, but we have no measure of it, of easy application and admitted accuracy, above the boiling point of mercury. Recourse has been had to the expansion of solids at high temperatures, and various pyrometers, or "measures of fire," have been proposed. Professor Daniel's pyrometer is a valuable instru-



ment of this kind, but it has not yet come into general use. Its indications result from the difference in the expansion by heat of an iron or platinum bar, and a tube of well-baked black-lead ware, in which the bar is contained. The metallic bar *a* is shorter than the tube, and a short plug of earthenware *b* is

placed in the mouth of the tube above the iron bar, and so secured by a strap of platinum foil and a little wedge, that it slides with difficulty in the tube. By the expansion of the metallic bar, the plug of earthenware is pushed outwards, and remains in its new position after the contraction of the metallic bar on cooling. The expansion of the iron bar thus obtained, is measured by adapting to the instrument an index, *c*, which traverses a circular scale, before and after the earthenware plug has been moved outwards by the expansion of the metallic bar. The degrees marked on the scale are in each instrument compared experimentally with those of the mercurial scale, and the ratio marked on the instrument, so that its degrees are convertible into those of Fahrenheit, (*Philosophical Transactions*, 1830-31.) An air thermometer, of which the bulb and tube were of metal, has also been employed to explore high temperatures. In the old pyrometer of Wedgwood, the degree of heat was estimated by the permanent contraction which is produced upon a pellet of pipe-clay; but the indications of this instrument are fallacious, and it has long gone out of use.

The applicability of the mercurial thermometer, to measure degrees of heat, depends upon two important circumstances, which involve the whole theory of the instrument:

1st. The hollow glass ball, with its fine tube of uniform bore, is a nice fluid measure. The ball and part of the stem being filled with a fluid, the slightest change in the bulk of the fluid, which may arise from the application of heat or of cold to it, is conspicuously exhibited by the rise or fall of the fluid column in the stem. No more delicate measure of the bulk of an included fluid could be devised.

2nd. It fortunately happens that the expansions of the fluid metal, mercury, which we can thus measure so accurately, are proportional to the quantities of heat which produce them. But the mode in which this is proved, requires a little attention. Suppose we had two reservoirs, one containing cold, and the other hot water. Plunge a thermometric bulb containing mercury first into the cold water, and mark at what point in the stem the mercury stands. Then plunge it into the hot water, and mark also the point to which the mercury now rises in the stem. We can obviously make a heat which will be half way exactly between the hot and cold water, by taking the same quantity of the hot and cold water and mixing them together.

Now, does this half heat produce a half expansion in mercury? On trial we find that it does. In the mixture of equal parts of the hot and cold water, the mercury stands exactly half way between the marks, supposing the experiment to be conducted with the proper precautions. This proves that the dilatations of mercury are proportional to the intensity of the heat which produces them. In the mercurial thermometer, therefore, quantities or degrees of expansion may be taken to indicate quantities or degrees of heat; and that is the principle of the instrument.

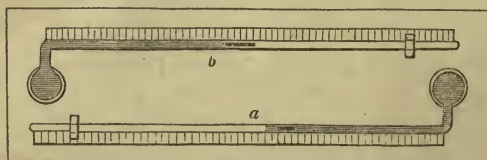
The same correspondence exists between the expansions of *air* and the quantities of heat which produce them. Indeed in the case of air, the correspondence is rigidly exact, while in the case of mercury it is only a close approximation. Thus Dulong and Petit found that the boiling point of mercury was,

as measured by mercury in a syphon	. . .	680°.
„ the air thermometer	. . .	662°.
„ mercury in glass, (Mr. Crichton)		660°.

A short table exhibiting the increasing rate of the expansions of mercury has already been given, but glass expands in a ratio increasing still more rapidly than this metal; so that the greater expansion of the mercury in the thermometer at high temperatures, is fortunately corrected by the increasing capacity of the glass bulb.

Fixed oils and spirits of wine do not deviate far from uniformity in their expansions, at least at low temperatures, and therefore are sometimes used as thermometric liquids.

Thermometers have been devised which indicate the highest and lowest temperature which has occurred between two observations, or are self-registering. Six's thermometer, which was



invented by Dr. Rutherford is of this kind. This instrument consists, properly speaking, of two thermometers,

one *a*, of spirit of wine, and the other *b* of mercury, which are placed in the position represented in the figure, their stems being in a horizontal direction. The thermometer *b* is intended to indicate the maximum temperature. It contains, in advance of the mercury, a short piece of iron wire, which the mercury carries forward with it in dilating, and which remains in its

advanced position, marking the highest temperature that has occurred, when the mercury withdraws. The minimum temperature is indicated by the spirit of wine thermometer *a*, which contains, immersed in the spirit, a small cylinder of ivory, which by a slight inclination of the instrument falls to the surface of the liquid without being able to pass out of it. When the thermometer sinks, the ivory is carried back in the spirit; but when the temperature rises, the alcohol only advances, leaving the ivory where it was. Its extremity most distant from the bulb then indicates the lowest temperature to which the thermometer had been exposed. Before another observation is made, the ivory must be brought again to the surface of the alcohol, by a slight percussion of the instrument.

Our notions of the range of temperature acquire all their precision from the use of the thermometer. Cold, for instance is allowed a substantial existence as well as heat, in popular language. What is cold? it is the absence of heat, as darkness is the absence of light. The absence of heat, however, is never complete but only partial. Water, after it is frozen into ice, cold as it is in relation to our bodies, has not lost all its heat, for it is easy to cool a thermometer far below the temperature of ice, and have it in such a condition as that it shall acquire heat, and be expanded by contact with ice; thus proving that the ice contains heat. Spirits of wine have not been frozen at the lowest temperature that has hitherto been attained; but even then this liquid possesses heat, and there is no doubt that if a sufficiently large portion of its heat were withdrawn it would freeze like other bodies. The following are interesting circumstances in the range of temperature:

—135°	Fahr.	Greatest artificial cold. Thilorier.
—121°	„	Solid compound of alcohol and carbonic acid melts.
—91°	„	Greatest artificial cold measured by Walker.
—58°	„	Temperature of planetary space. Fourier.
—60°	„	Greatest natural cold observed by Ross.
—55°	„	Greatest natural cold observed by Parry.
—47°	„	Sulphuric ether congeals.
—39°	„	Melting point of solid mercury.
—7°	„	A mixture of equal parts of alcohol and water freezes.

+7°	„	A mixture of one part of alcohol and three parts of water freezes.
+20°	„	Strong wine freezes.
+32°	„	Ice melts.
+50°	„	Medium temperature of the surface of the globe.
+52°	„	Mean temperature of England.
+98°	„	Heat of the human blood.
+150°	„	Wood-spirit boils.
+174°	„	Alcohol boils.
+212°	„	Water boils.
+442°	„	Tin melts.
+594°	„	Lead melts.
+662°	„	Mercury boils.
+980°	„	Red heat. Daniell.
+1141°	„	Heat of a common fire. Do.
+1869°	„	Brass melts. Do.
+2233°	„	Silver melts. Do.
+3479°	„	Iron melts. Do.

SPECIFIC HEAT.

Equal bulks of different substances, such as water and mercury, require the addition of different quantities of heat to produce the same change in their temperature. This appears evident from a variety of circumstances. If two similar glass bulbs, like thermometers, one containing mercury and the other water, be immersed at the same time in a hot water-bath, it will be found that the mercury bulb is heated up to the temperature of the water-bath in half the time that the water bulb requires; and if the two bulbs, after having both attained the temperature of the water-bath, be removed from it and exposed to the air, the mercury bulb will cool twice as rapidly as the other. These effects must arise from the mercury absorbing only half the quantity of heat which the water does in being heated up to the same degree in the water bath, and from having consequently only half the quantity of heat to lose in the subsequent cooling. Again, if we mix equal measures of water at 70° and 130°, the temperature of the whole will be 100°; or the hot measure of water, in losing thirty degrees, elevates the temperature of the cold measure by an equal amount. But if we

substitute for the hot water in this experiment an equal measure of mercury at 130° , on mixing it with the measure of water at 70° the temperature of the whole will not be 100° , but more nearly 99° . Here the mercury is cooled from 130° to 90° , or loses forty degrees of heat; which have been transferred to the water, but which raise the temperature of the latter only twenty degrees, or from 70° to 90° . To heat the measure of water at 70° to 100° , we must mix with it two, or a little more than two equal measures of mercury at 130° , although one measure of water at 130° would answer the purpose. If, therefore, *two* measures of mercury, by losing thirty degrees of temperature, heat up only *one* measure of water by thirty degrees, it follows that hot mercury possesses only half the heat of equally hot water; or that water requires double the quantity of heat that is required by mercury, to raise it a certain number of degrees. This is expressed by saying that water has twice the *capacity for heat* that mercury possesses.

It is more convenient to express the capacities of different bodies for heat, with reference to equal weights than equal measures of the bodies. On accurate trial, it is found that a pound of water absorbs thirty times more heat than a pound of mercury, in being heated the same number of degrees: the capacity of water for heat is, therefore, thirty times greater than that of mercury. The capacities of these two bodies are in the relation of 1000 to 33; and it is convenient to express the capacities for heat of all bodies, in relation to that of water as 1000. Such numbers are the *specific heats* of bodies.

The best method of determining the capacity for heat, consists in allowing different substances to cool the same number of degrees in circumstances which are exactly similar; to inclose them, for instance, in a polished silver vessel, containing the bulb of a thermometer in its centre, and to place this vessel under a bell-jar in which a vacuum is made. The time which the different substances take to cool, enables us to calculate the quantity of heat which they give out. By this exact method, Messieurs Dulong and Petit determined the capacity for heat of the following substances:

						Specific heat.
Water	1000
Sulphur	188
Glass	117

	Specific heat.
Iron	110
Copper	95
Zinc	93
Silver	56
Mercury	33
Platinum	31
Lead	29

The method of cooling gives results so exact, as to allow the detection of an increase of capacity with the temperature. The capacity of iron, when tried between 32° and 212° , as was the case with all the bodies in the table, was 110; but 115 between 32° and 392° , and 126 between 32° and 662° . It hence follows, that the capacity for heat, like dilatation, augments in proportion as the temperature is elevated. Dulong and Petit likewise established a relation between the capacity for heat of metallic bodies and the proportion by weight in which they combine with oxygen, or any other substance, which will again be adverted to.

Of all liquid or solid bodies, water has much the greatest capacity for heat. Hence the sea, which covers so large a proportion of the globe, is a great magazine of heat, and has a beneficial influence in equalizing atmospheric temperature. Mercury has a small specific heat, so that it is quickly heated or cooled, another property which recommends it as a liquid for the thermometer, imparting, as it does, great sensibility to the instrument.

The determination of the specific heat of gases is a problem involved in the greatest practical difficulties; so that notwithstanding its having occupied the attention of some of the ablest chemists, our knowledge on the subject is still of the most uncertain nature. It has been concluded by Delarive and Marcet,* and by Mr. Haycraft,† that the specific heat of all gases is the same for equal volumes. But this opinion has been controverted by Dulong,‡ and by Dr. Apjohn;§ and most chemists are now disposed to place more reliance upon the old experiments of Delaroche and Berard than upon any others

* Annales de Ch. et de Ph. t. 35, p. 5. and t. 41, p. 78.

† Edinburgh Phil. Trans. 1824.

‡ Annales de Ch. et de Ph. t. 41, p. 113.

§ Transactions of the Royal Irish Academy, 1837.

which have been subsequently published.* Their method was to transmit known quantities of the gases, heated to 212° in an uniform current, through a serpentine tube, surrounded by water, the temperature of which was observed, by a delicate thermometer at the beginning and end of the process. Their results are as follows :

Specific heat of gases referred to water.

	specific heat. same weight.		specific heat. same weight.
Water	1000	Nitrogen	275
Air	267	Nitrous oxide	237
Hydrogen	3294	Olefiant gas	421
Carbonic acid	221	Carbonic oxide	288
Oxygen	236	Steam	847

It will be observed, that the capacity for heat of steam is less than that of an equal weight of water. Hence, the specific heat of a body may change with its physical state. Delaroche and Berard likewise observed that the capacity of a gas is increased by its rarefaction. When the volume of a gas is doubled, by withdrawing half the pressure upon it, its specific heat is not quite so much as doubled. This is the reason why a gas becomes cold in expanding. In the expanded state it requires more heat to sustain it at its former temperature, from the augmentation which has occurred in its capacity. Air expanded into double its volume is cooled 40 or 45 degrees ; and it has its temperature raised to that extent by compression into half its volume ; suddenly condensed to one-fifth of its volume by a piston in a small brass cylinder, so much heat is evolved as to cause the ignition of a readily inflammable substance, such as tinder.

COMMUNICATION OF HEAT BY CONDUCTION AND RADIATION.

I. Conduction. When one extremity of a bar of iron is plunged into a fire, the heat passes through the bar in a gradual manner, being communicated from particle to particle, and after passing through the whole length of the bar, may arrive at the other extremity. Heat, when conveyed in this way, is said to be conducted.

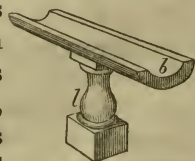
* Annales de Chimie, t. 75 ; or Annals of Philosophy, vol. ii.

In the case of solid substances, the phenomenon of the conduction of heat is so simple and familiar, that little need be said on the subject. Different solid substances vary exceedingly from each other in their power to conduct heat. Dense or heavy substances are generally good conductors, while light and porous bodies conduct heat imperfectly. Hence, the universal use of substances of the latter class for the purposes of clothing. Count Rumford observed that the finer the fabric of woollen cloth is, the more imperfectly does it conduct. The down of the eider-duck appears to be unrivalled in this respect. Bad conductors are also the most suitable for keeping bodies cool, protecting them from the access of heat. Hence, to preserve ice in summer, we wrap it in flannel. Among good conductors of heat, the metals are the best. The relative conducting power of several bodies is expressed by the numbers in the following table, from the experiments of Despretz.

Gold	1000	Tin	303.9
Silver	973	Lead	179.6
Copper	898	Marble	23.6
Platinum	381	Porcelain	14.2
Iron	374.3	Clay	11.4
Zinc	363		

Glass is an imperfect conductor, for we can fuse the point of a glass rod in a lamp, holding it within an inch of the extremity. On the contrary, we find it difficult to heat any part of a thick metallic wire to redness in a lamp, owing to the rapidity with which the heat is carried away by the contiguous parts.

Certain vibrations were observed by Mr. Trevelyan to take place between metallic masses having different temperatures, occasioning particular sounds, which appear to be connected with the conducting power of the metals.* Thus if a heated curved bar of brass *b*, be laid upon a cold support of lead *l*, of which the surface is flat, as represented in the figure, the brass bar, while communicating its heat to the lead, is thrown into a state of vibration, accompanied with a rocking motion and the production of a musical note, like that of the glass harmonicon. The motion of the brass bar appears to depend upon a certain repulsion existing between heated surfaces, enhanced in this case by the low

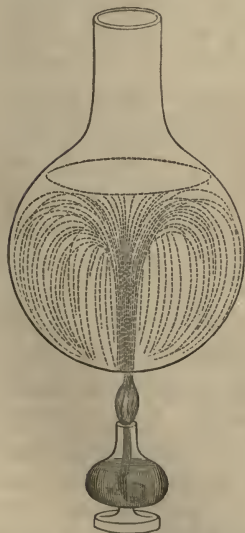


* Phil. Mag. 3d series, vol. iii, 321.

conducting power of the lead, which allows its surface to be strongly heated by the brass. Professor Forbes finds that the most intense vibrations are produced between the best conductors and the worst conductors of heat, the latter being the cold bodies.*

Our ordinary conceptions of the actual temperature of different bodies, are much affected by the conducting powers of these bodies. If we apply the hand, at the same time, to a good and to a bad conductor, such as a metal and a piece of wood, which are exactly of the same temperature by the thermometer, the good conductor will feel colder or hotter than the other, from the greater rapidity with which it conducts away heat from, or communicates heat to our body, according as the temperature of the metal and wood happens to be above or below that of the hand applied to them.

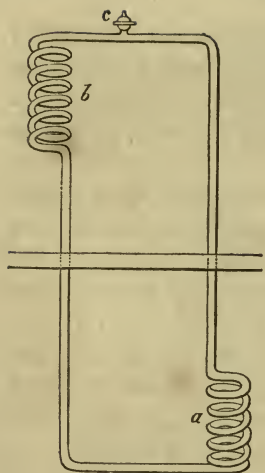
The diffusion of heat through liquids and gases is effected, in a great measure, by the motion of their particles among each other. When heat is applied to the lower part of a mass of liquid the heated portions become lighter than the rest, and ascend rapidly, conveying or carrying the heat through the mass of the fluid. In a glass flask, for instance, containing water, with which a small quantity of any light insoluble powder



has been mixed, a circulation of the fluid may be observed upon the application of the flame of a lamp to the bottom of the vessel, the heated liquid rising in the centre of the vessel, and afterwards descending near its sides, as represented in the annexed figure. But when heat is applied to the surface of a liquid, this circulation does not occur, and the heat is propagated very imperfectly downwards. It has even been doubted whether liquids conduct heat downwards at all, or indeed in any other way than by conveying it, as above described. It can be proved, however, that heat passes downwards in fluid mercury, and hence it is probable that all liquids possess a

slight conducting power similar to that of solids.

* Edin. Phil. Trans. vol. xii.



Let the endless tube represented in the accompanying figure be supposed to be entirely filled with water, and the heat of a fire be applied to the lower portion of it at *a*, which is twisted into a spiral form, the water will immediately be set in motion, and made to circulate through the tube, from the expansion and ascent of the portion in *a*, and the whole of the water in the tube will be brought in succession to the source of heat. The tube may be led into an apartment above *d*, and being twisted into another spiral at

b, a quantity of the heat of the circulating water will be discharged in proportion to the extent of surface of tube exposed. Water of a temperature considerably above 212° is made to circulate in this manner through a very strong drawn iron tube of about one inch in diameter, for the purpose of heating houses and public buildings. A slight waste of the water is found to occur, so that it is necessary to introduce a small quantity every few weeks by an opening and stopcock *c*, in the upper part of the tube. Tubes of larger calibre, with water circulating below the boiling point, are likewise much used for warming large buildings.

Air and gases are very imperfect conductors. Heat appears to be propagated through them almost entirely by conveyance, the heated portions of air becoming lighter, and diffusing the heat through the mass in their ascent, as in the case of liquids. Hence, in heating an apartment by hot air, the hot air should always be introduced at the floor or lowest part. The advantage of double windows for warmth depends, in a great measure, on the sheet of air confined between them, through which heat is very slowly transmitted. In the fur of animals and in clothing, a quantity of air is detained among the loose fibres, which materially enhances their non-conducting property. In dry air, the human body can resist a temperature of 250° without inconvenience, provided it is not brought into contact with good conductors at the same time.

Radiation of heat. Heat is also emitted from the surface of bodies in the form of rays, which pass through a vacuum, air,

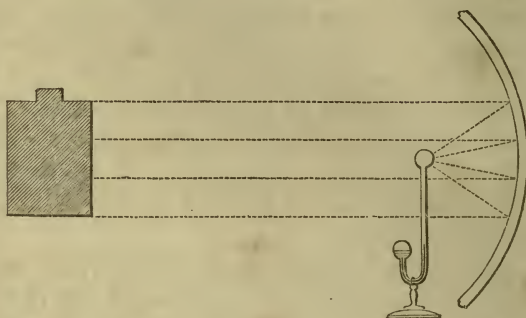
and certain other transparent media, with the velocity of light. It is not necessary that a body be heated to a visible redness to enable it to discharge heat in this manner. Rays of heat, unaccompanied by light, continue to issue from a hot body through the whole process of its cooling, till it sinks to the actual temperature of the air or surrounding medium. The circumstance that bodies suspended in a perfect vacuum cool rapidly and completely, without the intervention of conduction, places the fact of the dissipation of heat by radiation, at low temperatures, beyond a doubt.

The most valuable observations which we possess on this subject, were published by Sir John Leslie in his *Essay on Heat*, in 1804. Leslie proved that the rate of cooling of a hot body is more influenced by the state of its *surface* than by the nature of its *substance*. He filled a bright tin globe with hot water, and observed its rate of cooling in a room of which the air was undisturbed. A thermometer placed in the water cooled half way to the temperature of the apartment in 156 minutes. The experiment was repeated, after covering the globe with a thin coating of lamp-black. The whole now cooled to the same extent as in the first experiment in 81 minutes ; the rapidity of cooling being nearly doubled, merely by this change of surface.

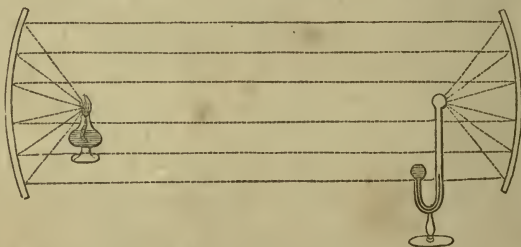
An experiment of Count Rumford is even more singular. Water, of the same temperature, was allowed to cool in two similar brass cylinders, one of which was covered by a tight investiture of linen, and the other left naked. The covered vessel cooled 10° in $36\frac{1}{2}$ minutes, while the naked vessel required 55 minutes ; or the covering of linen, like the coating of lamp-black greatly expedited the cooling, instead of retarding the escape of heat, as might have been expected. The cooling was accelerated in the same manner, when the cylinder was coated with black or white paint, or smoked by a candle.

In determining the radiating power of different surfaces, Leslie generally made use of square tin canisters, of which the surfaces were variously coated, and which he filled with hot water. Instead of watching the rate of cooling, as in the experiments already mentioned, he presented the side of a canister, having its surface in any particular condition, to a concave metallic mirror, which concentrated the heat falling upon it into a focus, where the bulb of an air-thermometer was placed

to receive it, as represented in the annexed figure. The differential thermometer answered admirably for this purpose, as from its construction it is unaffected by the temperature of the room, while the slightest change in the temperature of the focal spot is immediately indicated by it.



Two metallic mirrors were occasionally used in conducting these experiments. The mirrors being arranged so as to stand exactly opposite to each other, with their principal axes in the same line; when a lighted lamp or hot canister is placed in the focus of one mirror, the incident rays are reflected by that mirror against the other, and collected in its focus.



The following table exhibits the relative radiating power of various substances, with which the surface of the canister was coated, as indicated by the effect upon the differential thermometer:

Lamp black	100	Tarnished lead	45
Water by estimate	100+	Clean lead	19
Writing-paper	98	Iron, polished	15
Sealing-wax	95	Tin plate, gold, silver,	
Crown glass	90	copper	12
Plumbago	75		

It thus appears that lamp black radiates five times more of the heat of boiling water than clean lead, and eight times more than bright tin. The metals have the lowest radiating power, which arises from their brightness and smoothness. If allowed to tarnish, their radiating power is greatly increased. Thus the

radiating power of lead with its surface tarnished is 45, and with its surface bright, only 19; but glass and porcelain radiate most powerfully although their surface is smooth. When the actual radiating surface is metallic, it is not affected in a sensible manner by the substance under it. Thus, glass covered with gold leaf possesses the radiating power of a bright metal.

It appears, from the recent experiments of Dr. Bache, that the radiating power of any surface is not affected by its *colour*, at least in an appreciable degree. Hence, no particular colour of clothes can be recommended for superior warmth in winter. But the absorbent power of bodies for the heat of the sun depends entirely upon their colour.*

The faculty which different surfaces possess of absorbing or of reflecting heat radiated against them, is connected with their own radiating power. Those surfaces which radiate heat freely, such as lamp-black, glass, &c., also absorb a large proportion of the heat falling upon them, and reflect little of it; while surfaces which have a feeble radiating and absorbing faculty, such as the bright metals, reflect a large proportion, as they absorb little, and form the most powerful reflectors. So that the good absorbents are found at the top, and the good reflectors at the bottom of the preceding table. The efficiency of a reflector depending upon its low absorbing power, reflectors of glass are totally useless in conducting experiments upon radiant heat. Metallic reflectors remain cold, although they collect much heat in their foci.

These laws of the radiation of heat admit of some practical applications. If we wish to retard, as much as possible, the cooling of a hot fluid or other substance, in what sort of vessel should we inclose it? In a metallic vessel, of which the surface is not dull and sooty, but clean and highly polished; for it has been observed that hot water cools twice as fast in a tin globe of which the surface is covered with a thin coating of lamp-black, as in the same globe when the surface is bright and clean. Hence, the advantage of bright metallic covers at table, and the superiority of metallic tea-pots over those of porcelain and stoneware.

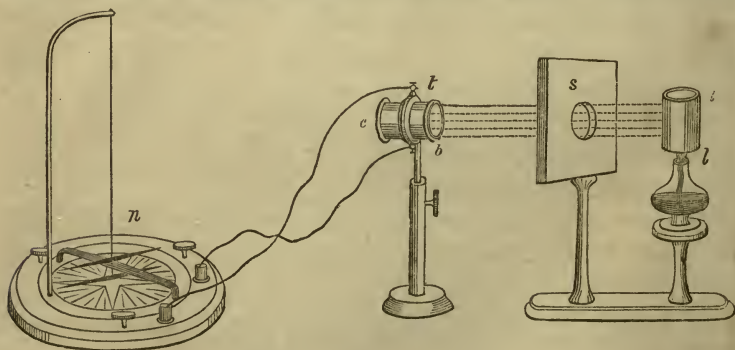
* Journal of the Franklin Institute, May and November 1835.

TRANSMISSION OF HEAT THROUGH MEDIA, AND THE EFFECT OF SCREENS.

It has been shewn by Dulong and Petit that hot bodies radiate equally in all gases, or exactly as they radiate in a vacuum. Hot bodies certainly cool more rapidly in some gases than in others, but this is owing to the mobility and conducting powers of the gases being different.

Light of every colour, and from every source, is equally transmitted by all transparent bodies in the liquid or solid form, but this is not the case with heat. The heat of the sun passes through any transparent body without loss, but of heat from terrestrial sources, a certain variable proportion only is allowed to pass, which increases as the temperature of the radiant body is elevated. Thus, it was observed by Delaroché that, from a body heated to 182° , only 1-40th of all the heat emitted passed through a glass screen: from a body at 346° , 1-16th of the whole; and from a body at 960° , so large a proportion as 1-4th appeared to pass through the screen. M. Melloni has, within the last few years, greatly extended our knowledge respecting the transmission of heat through media, in a series of the most profound researches.* In his experiments, he made use of the thermo-electric pile to detect changes of temperature, an instrument which in his hands exhibited a sensibility to the impressions of heat vastly greater than that of the most delicate mercurial, or air thermometer.

His instrument, or the thermo-multiplier, (see the annexed figure) consists of an arrangement of thirty pairs of bismuth and



* The complete series of Melloni's Memoirs given in Mr. R. Taylor's Scientific Memoirs, Nos. 1 and 3.

antimony bars contained in a brass cylinder, t , and having the wires from its poles connected with an extremely delicate magnetic galvanometer, n . The extremities of the bars at b being exposed to any source of radiant heat, such as the copper cylinder d , heated by the lamp l , while the temperature of the other extremities of the bars at c is not changed, a current of electricity passes through the wires from the poles of the pile, and causes the magnetic needle of the galvanometer to deflect. The quantity of electricity circulating increases in proportion to the difference of the temperatures of the two ends, b and c , that is in proportion to the quantity of heat falling upon b ; and the effect of this current of electricity upon the needle, or the deviation produced, is proportional to the quantity of electricity circulating, and consequently to the heat itself,—at least Melloni finds this correspondence to be exact through the whole arc, from zero to 20° , when the needle is truly astatic.

Melloni proved that heat, which has passed through one plate of glass, becomes less subject to absorption in passing through a second. Thus, of 1000 rays of heat from an oil flame, 451 rays being intercepted in passing through four plates of glass of equal thickness—

381	rays were intercepted by the first plate.
43	„ „ by the second.
18	„ „ by the third.
9	„ „ by the fourth.
<hr/>	
451	

The rays appear to lose considerably when they enter the first layers of a transparent medium; but that portion of heat, which has forced its passage through the first layers, may penetrate to a great depth. Transparent liquids are found to be less penetrable to radiant heat than solids.

The capacity which bodies possess of transmitting heat does not depend upon their transparency; or bodies are not at all *transparent to heat* in the same proportion that they are transparent to light. Thus, plates of the following transparent minerals, having a common thickness of 0.1031 of an inch, allowed very different proportions of the heat from the flame of an Argand oil-lamp to pass through them.

Of 100 incident rays, there were transmitted :—

By Rock-salt	92	rays.
„ Mirror glass	62	„
„ Rock-crystal	62	„
„ Iceland spar	62	„
„ Rock-crystal, smoky and brown	57	„
„ Carbonate of lead	52	„
„ Sulphate of barytes	33	„
„ Emerald	29	„
„ Gypsum	20	„
„ Fluor spar	15	„
„ Citric acid	15	„
„ Rochelle salt	12	„
„ Alum	12	„
„ Sulphate of copper	0	„

A piece of smoky rock-crystal, so brown that the traces of letters on a printed page covered by it, could not be seen, and which was fifty-eight times thicker than a transparent plate of alum, transmitted 19 rays, while the alum transmitted only 6. One substance which is perfectly opaque, a kind of glass used for the polarization of light, was found by Melloni to allow a considerable quantity of rays of heat to pass through it. He applies the term *diathermanous* to bodies which transmit heat, as *diaphanous* is applied to bodies which transmit light. Of all *diaphanous* or transparent bodies, water is in the least degree diathermanous. With the exception of the opaque glass referred to above, all diathermanous bodies belong also to the class of diaphanous bodies ; for those kinds of metal, wood and marble which totally obstruct the passage of light, obstruct that of heat also.

The proportion of heat from various sources which radiates through a plate of glass, 1-50th of an inch in thickness, was observed by Melloni to be as follows:

Of 100 rays from the flame

of an oil-lamp there were	.	54	transmitted,	46	absorbed.
„ „ red hot platinum,	37	„	63	„	
„ „ blackened copper,					
heated to 732° F.	12	„	88	„	
„ „ blackened copper					
heated to 212°	0	„	100	„	

But the power of transmission, in the case of rock-salt, is the same for heat from all these sources, or for heat of all intensities; 92 per cent of the incident heat being transmitted by that body, whether it be the heat radiated from the hand or from a bright Argand-lamp. Rock-salt stands alone in this respect among diathermanous bodies. This substance may be cut into lenses or prisms, and be used in concentrating heat of the very lowest intensity, or in decomposing it by double refraction, in the same manner as glass is employed in the case of the light of the sun. Indeed, rock-salt has become quite invaluable in researches upon the transmission of heat.

It thus appears that a body at different temperatures emits different species of rays of heat, which may be sifted or separated from each other by passing them through certain transparent media. They are all emitted simultaneously, and in different proportions by flame; but in heat from sources of lower intensity, some of them are always absent. The calorific rays of the sun are chiefly of the kind which passes through glass; but Melloni shows that the other species are not altogether wanting. The rays of heat emitted by the sun and other luminous bodies are quite different rays from the rays of light with which they are accompanied.

Of the Equilibrium of Temperature. When several bodies of various temperatures, some cold and some hot are placed near each other, their temperatures gradually approximate, and, after a certain period has elapsed, they are found all to be of one and the same temperature. To account for the production and continuation of this equilibrium of temperature, it is necessary to assume, that all bodies are at all times radiating heat in great abundance in all directions, although their temperature does not exceed or even falls below the temperature of the atmosphere. Hence, there is an incessant interchange of heat between neighbouring bodies; and a general equalisation of temperature is produced, when every object receives as much radiated heat as it emits.

This theory, which was first proposed by Prevost of Geneva, enables us to account for the apparent radiation of cold. Cold, we know, is a negative quality, being merely the absence of heat, and cannot therefore be radiated. Yet, when we place a lump of ice in the focus of a reflecting mirror, a thermometer in the focus of the opposite conjugate mirror is chilled. To

account for this phenomenon we must remember that the temperature of the thermometer is stationary, only so long as it receives as much heat as it radiates. It is in that state before the experiment is made with the ice; for the air or any object which may happen to be in the other focus is of the same temperature as the ball of the thermometer. But it is evident that the moment ice is introduced into one focus, less heat will be sent from that to the other focus, than was previously transmitted, and than is necessary to sustain the thermometer at a constant temperature. The thermometer ball, therefore, giving out as much heat as formerly and receiving less in return, must fall in temperature. This is an experiment in which the thermometer ball is in fact, the *hot body*.

The doctrine of the radiation of heat was very happily applied to account for the deposition of *Dew*. A considerable refrigeration of the surface of the ground below the temperature of the air resting upon it, amounting to 10 or 20 degrees, occurs every calm and clear night, and is caused by the radiation of heat from the earth (which is a good radiator) into empty space. Now on becoming colder than the air above it, the ground will condense the moisture of the air in contact with it, and be covered with dew. For the air, however clear, is never destitute of watery vapour, and the quantity of vapour which air can retain depends upon its temperature, air at 32°, for instance, being capable of retaining 1-150th of its volume of vapour while at 52° it can retain so much as 1-86th of its volume. The greatest difference between the temperature of the day and night in this country takes place in spring and autumn, and these are the seasons in which the most abundant dews are deposited.

That the deposition of dew depends entirely upon radiation is fully established by the following circumstances; 1°. It is on clear and calm nights only that dew is observed to fall. When the sky is overcast with clouds, no dew falls; for then the heat which radiates from the earth is returned by the clouds above, and prevented from escaping into space; so that the ground never becomes colder than the air. 2°. The slightest screen, such as a thin cambric handkerchief, stretched between pins, at the height of several inches above the ground, is sufficient to protect the objects below it from this chilling effect of radiation, and to prevent the formation of dew or of hoar-frost upon them. This fact was well known to gardeners, and they had long

availed themselves of it in protecting their tender plants from frost, before the laws of the radiation of heat came to be explained. 3°. Dr. Wells proved by numerous experiments that the quantity of dew which condenses on different objects exposed in the same circumstances, is proportional to the radiating power of those substances. Thus, when a polished plate of metal and a quantity of wool are exposed together in favourable circumstances, scarcely a trace of dew is to be observed on the metal, while a large quantity condenses in the wool, the latter substance being incomparably the best radiator, and therefore falling to a much lower temperature than the metal.

The same theory has been applied to explain a process for making ice followed by the native Indians near Calcutta. In that climate the temperature of the air rarely falls below 40° in the coldest nights; but the sky is clear, and a powerful radiation takes place from the surface of the ground. Hence, water contained in shallow pans imbedded in straw, is often sheeted over with ice by a night's exposure. The water is certainly cooled by radiation from its surface, and not by evaporation; for the process succeeds best when the pans are placed in shallow trenches dug in the ground, an arrangement which retards evaporation; and no ice forms in windy weather, when evaporation is greatest.

The morning frosts of autumn are first felt in sequestered situations, as in ravines closed on all sides, or along the low courses of rivers, where the cooling of the earth's surface by radiation is in the least degree checked by the movement of the air over it. These are also the very situations upon which the sun's rays produce the greatest effect in summer.

Reverting again to the subject of the conduction of heat through solid bodies, it may now be stated, that there is every reason to believe that heat is propagated, even in that case, in a manner not unlike radiation. Heat, in its passage through a bar of iron, is probably radiated from particle to particle; for the material atoms, of which the bar consists, are not supposed to be in absolute contact, although held near each other by a strong attraction. Radiation, as observed in air or a vacuum, may thus pass into conduction in the case of solids, without any breach of continuity in the natural law to which heat in motion is subject. Baron Fourier proceeds upon such an hypothesis in his mathematical investigation of the law of

cooling by conduction in solid bodies, and obtains expressions which agree with his experimental results.

We are now in a condition to advert with advantage to the equilibrium of the temperature of the earth. There can be no doubt of the existence, in this globe of ours, of a *central heat*. At a depth under the surface of the earth, not in general exceeding fifteen yards, the thermometer is perfectly stationary, not being affected by the change of the seasons ; but at greater depths, the temperature progressively rises. M. Cordier, to whom we are indebted for a most profound investigation of this interesting subject, considers the two following conclusions to be established by all the observations on temperature which have been made at considerable depths. 1st. That below the stratum where the annual variations of the solar heat cease to be sensible, a notable increase of temperature takes place as we descend into the interior of the earth. 2ndly. That a certain irregularity must be admitted in the distribution of the subterraneous heat, which occasions the progressive increase of temperature to vary at different places. Fifteen yards has been provisionally assumed as the average depth which corresponds to an increase of one degree Fahrenheit. This is about 116 degrees for each mile. Admitting this rate of increase, we have at a depth of $30\frac{1}{2}$ miles below the surface, a temperature of 3500° , which would melt cast iron, and which is amply sufficient to melt the lavas, basalts, and other rocks, which have actually been erupted from below in a fluid state. But this central heat has long ceased to affect the surface of the earth. Fourier demonstrates, from the laws of conduction, that although the crust of the globe were of cast iron, heat would require myriads of years to be transmitted to the surface, from a depth of 150 miles. But the crust of the globe is actually composed of materials greatly inferior to cast iron in conducting power. The temperature of the surface of the globe now depends upon the amount of heat which it receives from the sun, compared with the heat radiated away from its surface into free space. There is reason to believe that no material change has occurred in the quantity of heat received from the sun during the historical epoch. The radiation from the surface of the earth has its limit in the temperature of the planetary space in which it moves, which Fourier deduces, from calculation to be -58° , and which Schwanberg, from a calculation on totally different principles, estimates at $-58^{\circ}.6$, a very close coincidence. This low temperature

appears to be attained in the long absence of the sun during a polar winter, as Captain Parry found the thermometer to fall as low as -55° at Melville Island, and Ross more lately observed a temperature so low as -60° .

FLUIDITY AS AN EFFECT OF HEAT.

We have already adverted to one of the general effects of heat upon bodies, namely, its power of causing them to expand which demanded our earliest attention, as it involves the principle of the thermometer. But heat, besides effecting changes in the bulk, is capable of effecting changes in the *state* of bodies. Matter is presented to us in three very dissimilar states or forms, namely, in the solid, liquid, and gaseous forms. It is believed that no body is restricted to any one of these forms, but that the state of bodies depends entirely upon the temperature in which they are placed. In the lowest temperatures, they are all solid, in higher temperatures they are converted into liquids, and in the highest of all they become elastic gases. The particular temperatures at which bodies undergo these changes are exceedingly various, but they are always constant for the same body. The first effect then of heat on the state of bodies is the conversion of solids into liquids; or heat is the cause of fluidity.

Some substances, in liquefying, pass through an intermediate condition, in which it is difficult to say whether they are liquids or solids. Thus tallow, wax, and several other bodies, pass through every possible degree of softness before they attain complete fluidity. Such bodies, however, are in general mixtures of two or more substances, which crystallize imperfectly. But ice, and the great majority of bodies, pass immediately from the solid into the liquid state. The temperatures at which bodies undergo this change are exceedingly various:

Lead	melts at	612°	Olive oil	melts at	36°
Bismuth	„	476	Ice	„	32
Tin	„	442	Milk	„	30
Sulphur	„	232	Wines	„	20
Wax	„	142	Oil of turpentine	„	14
Spermaceti	„	112	Mercury	„	-39
Phosphorus	„	108	Liquid ammonia	„	-46
Tallow	„	92	Ether	„	-46
Oil of Anise	„	50			

If the bodies are in the fluid form, they freeze upon being cooled below the temperatures set against them.

It may be added, in reference to this table, first, that in certain circumstances, liquids can be cooled down several degrees below their usual freezing point before they begin to congeal. Thus we may succeed, by taking certain precautions, in cooling a small quantity of water, in a glass tube, so low as the temperature 8° , or even as 5° , without its freezing; that is, 24 or 27 degrees under its proper freezing point 32° . The water must be cooled without the slightest agitation, and no sand or angular body be in contact with it; for the instant any solid body is dropped into water cooled below its freezing point, or a tremor is communicated to it, congelation commences, and the temperature of the liquid starts up to 32° . But, on the other hand, we cannot heat a solid the smallest fraction of a degree above its proper melting point, without occasioning liquefaction. Hence it is not the freezing of water, but the melting of ice, which takes place with rigorous constancy at 32° Fahrenheit.

All salts dissolved in water have the effect of lowering the freezing temperature of that liquid. Common culinary salt appears to depress this point lower than any other saline body; and the effect appears to be very closely proportional to the quantity of salt in solution. A solution of 1 part of salt in 4 of water freezes at 4° , and sea water, which contains 1-30th of its weight of salt, freezes at 28° .

But the principal fact to be adverted to in liquefaction, is the disappearance of a large quantity of heat during the change. Heat pours into a body during its melting, without raising its temperature in the most minute degree. This heat, which enters the body and becomes insensible or latent, merely serves to melt the body. We are indebted to Dr. Black for this observation, which involves consequences of greater importance than any other announcement in the theory of heat.

Before Dr. Black's views were made known, fluidity was universally considered as produced by a very small addition to the quantity of heat which a body contains, when it is once heated up to its melting point; that a solid body, when it is changed into a fluid, receives no greater addition to the heat within it than is indicated and measured by the elevation of the mercury in the thermometer. But Dr. Black objected to this opinion, as inconsistent with many remarkable facts, when considered

properly. If we attend, for instance, to the manner in which ice and snow melt, when exposed to the air of a warm room, we can perceive, that however cold they may be at first, they are soon heated up to their melting point, and begin at their surface to be changed into water. Now if the complete change of these bodies into water required only the farther addition of a very small quantity of heat, a mass of them, though of considerable size, ought all to be melted in a few minutes or seconds more, the heat continuing to be communicated from the air around. But masses of ice and snow are well known to melt with extreme slowness, especially if they be of a large size, as are those collections of ice and wreaths of snow, that are formed in some places during winter. These, after they begin to melt, often require many weeks of warm weather, before they are totally dissolved into water. The slow manner in which ice melts in ice houses is also familiarly known to all.

By examining what happens in these cases, it may easily be perceived that a very great quantity of heat must enter the melting ice, to form the water into which it is changed, and that the length of time necessary for the collection of so much heat from surrounding bodies, is the reason of the slowness with which the ice is liquefied. When melting ice is suspended in warm air, the entrance of heat into it is made sensible by a stream of cold air descending constantly from the ice, which may be perceived by the hand. It is, therefore, evident that the melting ice receives heat very fast, but the only effect of this heat is to change it into water, which is not in the least sensibly warmer than the ice was before. A thermometer applied to the drops or small streams of water as they come immediately from the melting ice, will point to the same degree as when applied to the ice itself. A great quantity of the heat, therefore, which enters into the melting ice, has no other effect than that of giving it fluidity. The heat appears to be absorbed or concealed within the water, and cannot be detected by the thermometer.

When ice is melted by means of warm water, this absorption of heat is made exceedingly obvious. Thus on mixing a pound of water at 172° with a pound of snow at 32° , the snow is all melted, and the mixture is two pounds of water of the temperature of 32° . In being cooled down from 172° to 32° , the hot water loses 140 degrees of heat, which convert the snow into

water, indeed, but produce no rise of temperature in the mixture above the 32 degrees originally possessed by the snow.

Dr. Black proved that the heat which disappears in this manner is not extinguished or destroyed, but remains latent in the water so long as it is fluid, and is extricated again when it freezes.

In water that has been cooled below its usual freezing point, when the congelation is once determined, quantities of icy spiculæ are produced in proportion to the depression of temperature, whilst at the same instant the temperature of ice and water starts up to 32°. The heat which thus appears was previously latent in that portion of the water which is frozen. The same disengagement of latent heat may be conveniently illustrated by means of a supersaturated solution of sulphate of soda, formed by dissolving, at a high temperature, three pounds of the salt in two pounds of water. When this liquid is allowed to cool undisturbed and with a few drops of oil on its surface, it remains fluid, although containing a much greater quantity of salt in solution than the water could dissolve at the temperature to which it has fallen. But the suspended congelation of the salt being determined by the introduction of any solid substance into the solution, the temperature then often rises 30 and even 40 degrees, while crystals of sulphate of soda shoot rapidly through the liquid.

Wax, tallow, sulphur and all other solid bodies are melted in the same manner as water, by the assumption of a certain dose of heat. The latent heat which the following substances possess in the fluid form was, with the exception of water, determined by Dr. Irvine.

					Latent heat.
Water	140 degrees
Sulphur	145 „
Lead	162 „
Bees' wax	175 „
Zinc	493 „
Tin	500 „
Bismuth	550 „

Even in the solid form certain bodies admit of a variation in their structure and properties from the assumption or loss of latent heat. Dr. Black made it appear probable that metals owe their malleability and ductility to a quantity of latent heat

combined with them. When hammered they become hot from the disengagement of this heat, and at the same time become brittle. Their malleability is restored by heating them again in a furnace. Sugar, it is well known, may exist as a transparent and colourless body, with the physical properties of glass, or as a white and opaque, because a granular or crystalline mass. The transition from the glassy to the granular state is attended by a very remarkable evolution of heat, which appears to have escaped the notice of scientific men. If melted sugar be allowed to cool to about 100° , and then, while it is still soft and viscid, be rapidly and frequently extended and doubled up, till at last it consists of threads, the temperature of the mass quickly rises so as to become insupportable to the hand. Applying the thermometer, I found the temperature of a considerable mass to rise from 105° to 175° in less than two minutes. After this liberation of heat, the sugar on again cooling is no longer a glass, but consists of minute grains, and has a pearly lustre. The same change may occur in a gradual manner, as when a clear stick of barley-sugar becomes white and opaque in the atmosphere; but then we have no means of observing the escape of the latent heat on which the change depends. It may be inferred that glass itself, like transparent barley-sugar, owes its peculiar constitution and properties to the permanent retention of a certain quantity of latent heat. Of this heat glass can be deprived, by keeping it long in a soft state; it then becomes granular, and passing into the condition of Reaumur's porcelain, loses all the characters of glass.

It is not unlikely that the *dimorphism* of a body, or its property to assume two different crystalline forms, may likewise depend upon the retention of a certain quantity of latent heat by the body in the one form and not in the other. Thus sulphur assumes two forms, one on cooling from a state of fusion by heat, another in crystallizing at a lower temperature, and probably with the retention of less latent heat, from a solution of sulphuret of carbon; in charcoal and plumbago, again, we have carbon which has assumed the solid form at a high temperature, and possibly with the fixation of a quantity of latent heat which does not exist in the diamond, another form of the same body.

When a solid body is melted by the intervention of some affinity, without heat being applied to it, cold is generally produced. Thus most salts occasion a reduction of temperature,

in the act of dissolving in water, which requires them to become fluid. Nitre, for instance, cools the water in which it is dissolved 15 or 18 degrees. A mixture of five parts of sal ammoniac and five of nitre, both finely powdered, dissolved in nineteen parts of water, may reduce its temperature from 50° to 10° , or considerably below the freezing point of pure water. These salts are necessitated, by their affinity for water, to dissolve when mixed with it and to become fluid, a change which implies the assumption of latent heat. Most of our artificial processes for producing cold are founded upon this disappearance of heat during liquefaction. A very convenient process for freezing a little water, without the use of ice, is to drench finely powdered sulphate of soda with the undiluted hydrochloric acid of the shops. The salt dissolves to a greater extent in this acid than in water, and the temperature may sink from 50° to 0° . The vessel in which the mixture is made becomes covered with hoar frost, and water in a tube immersed in the mixture is speedily frozen.

The same affinity between salts and water may be taken advantage of to cause the liquefaction of ice, as when common salt is strewed upon pavements covered with ice, to melt it. On mixing snow with a third of its weight of salt, the snow is melted, and the temperature sinks nearly to 0° . It was in this way that Fahrenheit is supposed to have obtained the zero of his scale. Ices for the table are always made in summer by mixing roughly pounded ice and salt together, and immersing the cream, or other liquid to be frozen, contained in a thin metallic pan, in the cold brine which is produced by the melting of the ice.

The liquefaction of snow by means of the salt, chloride of calcium, occasions a still greater degree of cold. To prepare this salt, marble or chalk is dissolved in hydrochloric acid, and the solution evaporated by a temperature not exceeding 300° . It should be stirred, as it becomes dry at this temperature; and is obtained in a crystalline powder, being the combination of chloride of calcium with two atoms of water. When three parts of this salt are mixed with two of dry snow, the temperature is reduced from 32° to -50° . In attempting to freeze mercury by means of this mixture, it is advisable to make use of not less than three or four pounds of the materials. When the materials are divided, and the mercury is first cooled consider-

ably by one portion, it rarely fails in being frozen when transferred into another portion of the mixture. For producing still more intense degrees of cold, the evaporation of highly volatile liquids, of fluid carbonic acid, for instance, affords the most efficient means.

VAPORIZATION.

We have now to consider the second general effect of heat : vaporization, or the conversion of solids and liquids into vapour. Vapours, of which steam is the most familiar to us, are light, expansible, and generally invisible gases, resembling air completely in their mechanical properties, while they exist, but subject to be condensed into liquids or solids by cold. Water undergoes a great expansion when converted into steam, a cubic inch of water becoming, in ordinary circumstances, a cubic foot of steam ; or more strictly, one cubic inch of water, when converted into steam, expands into 1694 cubic inches.

This change, like fluidity, is produced by the addition of heat to the body which undergoes it. But a much larger quantity of heat enters into vapours than into liquids, into steam than into water. If over a steady fire a certain quantity of ice-cold water requires one hour to bring it to the boiling point, it will require a continuance of the same heat for five hours more to boil it off entirely. Yet liquids do not become hotter after they begin to boil, however long, or with whatever violence, the boiling is continued : for if a thermometer be plunged into water, and the point marked where it stands at the beginning of the boiling, it will be found to rise no higher, although the boiling be continued for a long time.

This fact is of importance in domestic economy, particularly in cookery ; and attention to it would save much fuel. Soup, &c. made to boil in a gentle way, by the application of a moderate heat, are just as hot as when they are made to boil on a strong fire with the greatest violence ; when water in a boiler is once brought to the boiling point, the fire may be reduced, as having no farther effect in raising its temperature, and a moderate heat being sufficient to preserve it.

The steam from boiling water, when examined by the thermometer, is found to be no hotter than the water itself. What then becomes of all the heat which is communicated to

the water, since it is neither indicated in the steam nor in the water? It enters into the water, and converts it into steam, without raising its temperature. As much heat disappears as is capable of raising the temperature of the portion of water converted into steam 1000 degrees, or what is the same thing, as would raise the temperature of one thousand times as much water by one degree. This is now generally assumed to be the amount of the latent heat of steam. Dr. Black found it to be about 960 degrees, Mr. Watt 940 degrees, and Lavoisier rather more than 1000 degrees.

Several circumstances may be remarked during the occurrence of this change in water. On heating water gradually in a vessel we first observe minute bubbles to form in the liquid and rise through it, which consist of air. As the temperature increases, larger bubbles are formed at the bottom of the vessel, which rise a little way in the liquid, and then contract and disappear, producing a hissing or simmering sound. But, as the heating goes on, these bubbles, which are steam, rise higher and higher in the liquid, till at last they reach its surface and escape, producing a bubbling agitation, or the phenomenon of *ebullition*. The whole process of boiling is beautifully seen in a glass vessel. It will be remarked that steam itself is invisible; it only appears when condensed again into minute drops of water by mixing with the cold air.

It was first observed by Guy-Lussac, that liquids are converted more easily into vapour when in contact with angular and uneven surfaces, than when the surfaces which they touch are smooth and polished. He also remarked that water boils at a temperature two degrees higher in glass than in metal; so that if into water, in a glass flask, which has ceased to boil, we drop a twisted piece of cold iron wire, the boiling is resumed: it is only in vessels of metal that the boiling point is regular, and should be taken in graduating thermometers. It has lately been remarked by Mr. Scrymgeour, of Glasgow, that if oil be present with water, the boiling point of the water is raised a few degrees, in any kind of vessel. The reason why water, in these circumstances, does not pass into vapour at its usual boiling point, is not distinctly understood. The water appears to be in a precarious state of equilibrium, as in the other analogous case, when cooled with caution in a smooth glass vessel considerably under its usual freezing point. The

introduction of an angular body into the water is sufficient, in either instance, to induce the suspended change. The same irregular deviation of the boiling point in glass vessels, takes place in other liquids as well as water, and in some of them to a much greater extent.

There is a curious circumstance in regard to boiling, which is a matter of common observation in some shape or other. When a little water (a few drops) is thrown into a metallic cup, hotter than the boiling point of water, the hotter the cup is, the less rapidly does the water boil away. We should expect the reverse, or that the hotter the metallic cup, the more quickly would the water be dissipated. The cause of the phenomenon appears to be this. Water exhibits an attraction for the surface of almost all solids at low temperatures, and wets them. Fluid mercury exhibits the opposite property, or a repulsion for most surfaces. This attraction of water for surfaces brings it into the closest contact with them, and greatly promotes the communication of heat by a heated vessel to the water contained in it. But heat appears to develop a repulsive power in bodies, and it is probable that above a particular temperature the heated metal no longer possesses this attraction for water. The water, not being attracted to the surface of the hot metal, and induced to spread over it, is not rapidly heated, and therefore boils off slowly. A rude method of judging of the degree of heat is founded on the same principle, and is seen familiarly exemplified in the laundry. The heat of the smoothing iron is judged of by its effects upon a drop of saliva let fall upon it. If the drop do not boil, but run along the surface of the metal, the iron is considered sufficiently hot; but if the drop adheres and is rapidly dissipated, the temperature is considered low.

The temperature at which any liquid boils is not fixed (like the melting point of solids), but depends entirely upon a particular circumstance,—the degree of pressure to which the liquid is at the time subject. Liquids are in general subject to the pressure of the atmosphere; for although the air is an exceedingly light substance, being 815 times lighter than water, yet by reason of its great quantity and height, it comes to weigh with considerable force upon the earth. This is called the atmospheric pressure, and amounts to no less than fifteen pounds upon each square inch of surface. The force with

which air presses upon a man of ordinary size has been estimated at fifty tons ; yet, from all the cavities of the animal frame being filled with equally elastic air, we support this great pressure without being sensible of it ; indeed, we should suffer the greatest inconvenience from its sudden removal. Now the pressure of the atmosphere is not always the same at the same place, but is found by the barometer to vary within the limits of one tenth of the whole pressure. This difference affects the boiling point to the extent of $4\frac{1}{2}$ degrees. Thus, when the height of the mercury in the barometer is expressed by the numbers in the first column, water boils at the temperatures placed against them in the second column.

Barometer in inches of mercury	water boils
27.74	208°
28.29	209
28.84	210
29.41	211
29.8	212
30.6	213

It appears, from this table, that for every inch of variation in the barometer, the boiling point of water varies 1. 76 degree. And consequently a rise or fall in the barometer of 0. 1 inch, raises or lowers the boiling point 0. 176 degree. On this account the pressure of the atmosphere must be attended to in fixing the boiling point of water on thermometers. Water boils at 212°, only when the pressure of the atmosphere is equivalent to a column of 29. 8 inches mercury.

The pressure of the atmosphere will be greatest at the level of the sea, and will diminish as we ascend to any height above it, for then we have less of the atmosphere above and pressing upon us, part of it being below us. Hence, water boils on the tops of mountains at a considerably lower temperature than at their bases. On the top of Mount Blanc, which is the pinnacle of Europe, water was observed by Saussure to boil at 184°. In deep pits, on the other hand, water requires a higher temperature to boil it, than at the surface of the earth. An instrument has been constructed for ascertaining the heights of mountains on this principle. It consists essentially of a thermometer, graduated with great care about the boiling point of water, by means of which the temperature at which water boils at different altitudes can be ascertained with minute accuracy.

A difference of one degree of temperature is occasioned by an ascent of 530 feet.

When the pressure on liquids is removed by artificial means, they boil at greatly reduced temperatures. This may be done by placing them under the receiver of an air-pump, and exhausting. When the whole air is withdrawn, liquids in general boil about 145 degrees under the temperature which they require to make them boil when subject to the atmospheric pressure. In a good vacuum water will boil at 67° . This fact is also illustrated by a simple experiment, which any one may perform. A flask containing boiling water, is closed with a cork while the upper part is filled with steam. The boiling in the flask may be renewed by plunging it into cold water; and the colder the water the brisker will the ebullition become. But the boiling is instantly checked by removing the flask from the cold water and immersing it in very hot water. On corking the flask, the ebullition ceased from the pressure exerted by the confined steam upon the surface of the hot water; but on plunging the flask into cold water, this steam was condensed, and the water began to boil under the reduced pressure. On removing the flask to the hot water, the steam above ceased to be condensed, and by its pressure stopped the boiling. On the other hand, in a Papin's digester, which is a tight and strong kettle with a safety valve, water may be raised to 3 or 400° without ebullition; but the instant that this great pressure is removed, the boiling commences with prodigious violence.

The facility with which liquids boil under reduced pressure is frequently taken advantage of in the arts, in concentrating liquors which would be injured in flavour or colour by the heat necessary to boil them under the pressure of the atmosphere. The late Mr. Howard applied this principle in concentrating syrup of the sugar, which is apt to be browned when made to boil under the usual pressure. He thus boiled syrup at 150° applying heat to it in a pan covered by an air-tight lid, and pumping off the air and steam from the upper part of the pan by means of a steam-engine. This was the most essential part of his patent process, by which nearly the whole of the loaf sugar consumed in this country, has been manufactured for several years.

In the same apparatus vegetable infusions may be inspissated, or reduced to the state of extracts, for medical purposes with

great advantage. When an extract is prepared in the ordinary way, by boiling down an infusion or expressed juice in an open vessel under atmospheric pressure, a considerable and variable proportion of the active principle is always destroyed by the high temperature and exposure to the air. But the extract is not injured when the infusion or juice is evaporated at a low temperature, and without access of air, and is generally found to be a more active medicine.

The temperatures at which different liquids are converted into vapour are exceedingly various ; but other things remaining the same, the boiling temperature is constant for any particular liquid. The following table exhibits the boiling points of a few liquids, in which that point has been determined with precision.

	Boiling point.
Hydro-chloric ether	52°
Sulphuric ether	96
Bisulphuret of carbon	116
Ammonia, (sp. gr. 0.945)	140
Alcohol, (sp. gr. 0.798)	172
Water	212
Nitric acid, (sp. gr. 1.42)	248
Crystallized chloride of calcium	302
Oil of turpentine	314
Naphtha	320
Phosphorus	554
Sulphuric acid, (sp. gr. 1.843)	620
Whale oil	630
Mercury	662

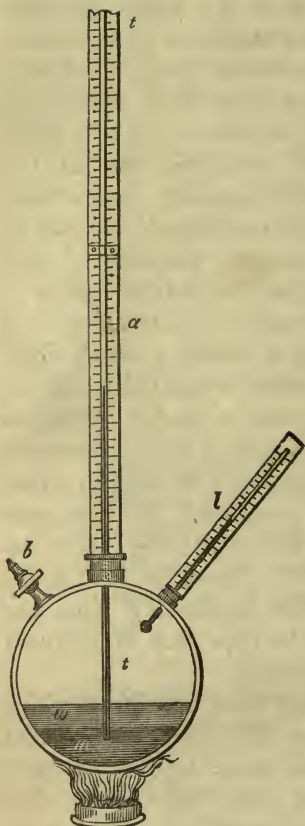
The boiling point of water is uniformly elevated, by the solution of salts in the fluid ; but much more so by some salts than others. Tables have been constructed of the boiling points of saline liquors, which are of useful application when we wish to maintain a steady temperature somewhat above 212°. Thus, water saturated with common salt, (100 water to 30 salt,) boils at 224° ; saturated with nitrate of potash, (100 water to 74 salt,) it boils at 238° ; saturated with chloride of calcium, at 264°.

When steam from water is confined, it increases in temperature and acquires great force, and the experiment can only be performed with safety in a boiler possessed of a safety valve.

This is a small lid in the upper part of the boiler, properly loaded, according to the force of the steam to be generated. The steam of boiling water occasions a severe scald, if allowed to condense upon the body. But when steam from water under pressure, or "high pressure" steam, which may be of a much higher temperature than boiling water, issues into the air, the hand may be directly exposed to it with impunity; and a thermometer placed in it, shows that its temperature is greatly below that of boiling water. This singular property of high pressure steam is connected with the great expansion which it undergoes on escaping into the air from the vessel in which it was confined; elastic bodies having a tendency when compressed to fly asunder, not only to their original dimensions, but beyond them. The steam is greatly expanded and at the same time mixed with air, which prevents it from afterwards collapsing. Now after being incorporated with several times its bulk of air, steam is not easily condensed, but becomes low-pressure steam, and may have its condensing point reduced from above 212° to 120° or 130° . Hence the heat which it is capable of communicating, while condensing upon the hand held in it, is of much less intensity than that of ordinary steam, and inadequate to occasion scalding.

Steam, when heated by itself, apart from the liquid which produced it, does not possess a greater elasticity than an equal bulk of air confined and heated to the same degree, and may be heated to redness, without acquiring great elastic force. But if water be present, then more and more steam continues to rise, adding its elastic force to that of the vapour previously existing, so that the pressure becomes excessive.

The elastic force of steam at temperatures above 212° is determined by heating water in a stout globular vessel containing mercury *m*, (see Figure) and water *w*, and having a long glass tube *tt*, screwed into it, open at both ends, and dipping into the mercury, having a scale *a*, divided into inches applied to it. The globular vessel has two other openings, into one of which a stopcock *b* is screwed, and into the other a thermometer *l*, having its bulb within the globe. The water is boiled in this vessel for some time, with the stopcock open, so as to expel all the air. On shutting the stopcock, and continuing the heat, the temperature of the interior, as indicated by the thermometer, now rises above 212° , at which it was



stationary while the steam generated was allowed to escape. The steam in the upper part of the globe becomes denser, more and more steam being produced, and forces the mercury to ascend in the gauge tube, *t t* to a height proportional to the elastic force of the steam. The height of the mercurial column may be taken to express the elastic force or pressure of the steam produced at any particular temperature above 212° . The weight of the atmosphere itself is equivalent to a column of mercury of 30 inches, and this pressure has been overcome by the steam at 212° , before it began to act upon the mercurial gauge. For every thirty inches that the mercury is forced up in the gauge tube by the steam, it is said to have the pressure or elastic force of another atmosphere. Thus, when the mercury in the tube stands at thirty inches, the steam is said to be of two atmospheres; at 45 inches, of two and a half atmospheres; at 60

inches, of three atmospheres, and so on.

Experiments have been made on the elastic force of steam by Professor Robinson, Mr. Southern, Mr. Watt, Dr. Ure, and others; but all preceding results have been superseded by those of a commission of the French Academy, appointed by the French government to investigate the subject, from its importance in connexion with the steam engine. Their results, which are expressed in the following table, were obtained by experiment, up to a pressure of 25 atmospheres. The higher pressures were calculated by extending the progression observed at lower temperatures.

Elasticity of steam taking atmospheric pressure as unity.	Temp. Fahr.	Elasticity of steam taking atmospheric pressure as unity.	Temp. Fahr.
1	212.0	13	380.66
1½	233.96	14	386.94
2	250.52	15	392.86
2½	263.84	16	398.48
3	275.18	17	403.82
3½	285.08	18	408.92
4	293.72	19	413.78
4½	300.28	20	418.46
5	307.5	21	422.96
5½	314.24	22	427.28
6	320.36	23	431.42
6½	326.26	24	435.56
7	331.70	25	439.34
7½	336.86	30	457.16
8	341.78	35	472.73
9	350.78	40	486.59
10	358.88	45	491.14
11	366.85	50	510.60
12	374.00		

Some curious experiments were made by M. Cagnard de la Tour on the vapour from various liquids at very high temperatures, and under great pressures. He filled a small glass tube in part with ether, alcohol, or water, and sealed it hermetically. The tube was then exposed to heat, till the liquid passed entirely into vapour. Ether became gaseous in a space scarcely double its volume at a temperature of 320°, and the vapour exerted a pressure of no more than 38 atmospheres. Alcohol became gaseous in a space about thrice its volume at the temperature 404°½, with a pressure of about 139 atmospheres. Water acted chemically on the glass, and broke it; but adding a little carbonate of soda to it, the water became gaseous in a space four times its volume at the temperature at which zinc melts, or about 648°. These results are singular, in so far as the pressure or elastic force of the vapours proves to be much smaller than that which corresponds with their calculated density. It thus appears that highly compressed vapours lose a portion of their elasticity, or yield more to a certain pressure than air, by calculation, would do.

The latent heat of the vapours of several other bodies besides water has been determined, and found to have a relation to the volumes of the vapours. Thus, when equal weights of water and oil of turpentine are converted into vapour under the same pressure, the quantity of heat rendered latent by the turpentine vapour is not more than one-fifth of the latent heat assumed by the water vapour; but the bulk of the latter vapour is about five times greater than that of the former. The table below exhibits the latent heat of equal weights of several vapours, as ascertained by Dr. Ure. He distilled, in all cases, 200 grains of the liquid, from a small retort, and condensed the vapour in a thin glass globe, surrounded with a certain quantity of water at a known temperature, contained in a glass basin. To prevent the air from exercising an influence on the temperature of the water in the basin, care was taken that the water should be three or four degrees below the temperature of the air at the beginning of the experiment, while it was not afterwards heated more than the same number of degrees above the atmospheric temperature by the condensation of the vapour. A thermometer of great delicacy was continually moved through the water, and its indications were read off to small fractions of a degree. The latent heat of each vapour was of course proportional to the rise of temperature which occurred in the condensing water.

Equal weights.	Latent heat.
Vapour of water	1000 degrees.
Alcohol (specific gravity 0.825).	457 „
Ether (boiling point 112°)	313 „
Petroleum	184 „
Oil of turpentine	184 „
Nitric acid (specific gravity 1.494)	550 „
Liquid ammonia (specific gravity 0.978)	866 „
Vinegar (specific gravity 1.007)	903 „

If the latent heat of different vapours be proportional to their volume, as these numbers seem to indicate, the same bulk of vapour will be produced from all liquids with the same expenditure of heat, and hence there can be no advantage in substituting any other liquid for water, as a source of vapour, in the steam engine.

The latent heat of the vapour of water itself increases with its rarity at low temperatures, and diminishes with its increasing density at high temperatures. Water may easily be made to

boil in a vacuum at the temperature of 100° , but the steam produced is much more expanded and rare than that produced at 212° , and has a greater latent heat. Hence there is no fuel saved by distilling in vacuo. It has been shown, by Mr. Sharpe of Manchester, that whatever be the temperature of steam, from 212° upwards, if the same weight of it be condensed by water, the temperature of the water will always be raised the same number of degrees; or the latent and sensible heat of steam, added together, amount to a constant quantity. We may hence deduce a simple rule for ascertaining the latent heat of steam at any particular temperature. The sensible heat of steam at 212° may be assumed as 212 degrees neglecting the heat which it has below zero Fahrenheit, and the latent heat of such steam is 1000 degrees, of which the sum is 1212 degrees. To calculate the latent heat of steam at any particular temperature above 212° , subtract the sensible heat from this constant number 1212. Thus the latent heat of steam at 300° is $1212 - 300$, or 912 degrees. The same relation between the latent and sensible heat of vapour appears to exist at temperatures below 212° , and we may, therefore, calculate the latent heat of vapour, below that temperature, by the same rule.

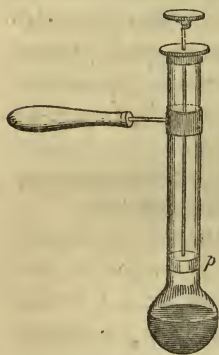
Temperature.				Latent heat of equal weights of steam.
0°	.	.	.	1212 degrees
32	.	.	.	1184 "
100	.	.	.	1112 "
150	.	.	.	1062 "
242	.	.	.	1000 "
250	.	.	.	962 "

The latent heat of other vapours, such as that of alcohol, ether, and oil of turpentine, has been found by Despretz to vary according to the same law.

From the large quantity of heat which steam possesses, and the facility with which it imparts it to bodies colder than itself, it is much used as a vehicle for the communication of heat. The temperature of bodies heated by it can never be raised above 212° ; so that it is much preferable to an open fire for heating extracts and organic substances, all danger of empyreuma being avoided. When applied to the cooking of food, the steam is generally passed into a shallow tin box, in the upper surface of which are cut several round apertures, of such sizes as admit exactly the pans with the materials to be heated. The pans are thus surrounded by steam, which condenses upon them

with great rapidity, till their temperature rises to within a degree or two of 212° . For some purposes, a pan containing the matters to be heated is placed within another and similar larger one, and steam admitted between the two vessels. Manufactured goods also are often dried by passing them once over a series of metallic cylinders, or square boxes filled with steam. Factories are now very generally heated by steam, conveyed through them in cast iron pipes. It has been found by practice that the boiler to produce steam for this purpose, must have one cubic foot of capacity for every 2000 cubic feet of space to be heated to a temperature of 70° or 80° ; and that of the conducting steam pipe, one square foot of surface must be exposed for every 200 cubic feet of space to be heated.

The expansion of water into steam is used as a moving power in the steam engine. The application is made upon two different principles, both of which may be illustrated by the little instrument depicted on the margin. It consists of a glass tube,

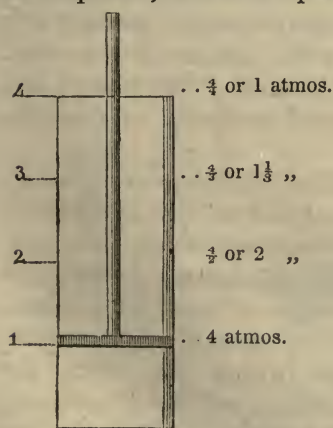


about an inch in diameter, slightly expanded into a bulbous form at one extremity, and open at the other; a piston is made, by twisting tow about the end of a piece of straight wire, which must be fitted tightly in the tube by the use of grease. Upon heating a little water in the bulb below the piston, steam is generated, which raises the piston to the top of the cylinder. Here the simple elastic force of the steam is the moving power; and in this manner steam

is employed in the high pressure engine. The greater the load upon the piston, and the more the steam is confined, the greater does its elastic force become. Again, the piston being at the top of the cylinder, if we condense the steam with which the cylinder is filled, by plunging the bulb in cold water, a vacuum is produced below the piston, which is now forced down to the bottom of the cylinder by the pressure of the atmosphere. In this second part of the experiment, the power is acquired by the condensation of the steam, or the production of a vacuum; and this is the principle of the common condensing engine. In the first efficient form of the condensing engine (that of Newcomen) the steam was condensed by injecting a little cold water below the piston, which then descended, from the pressure of the atmosphere upon its upper surface,

exactly as in the instrument. But Mr. Watt introduced two capital improvements into the construction of the condensing engine; the first was, the admitting steam, instead of atmospheric air, to press down the piston through the vacuous cylinder, which steam itself could afterwards be condensed, and a vacuum be produced above the piston, of which the same advantage might be taken as of the vacuum below the piston. The second was, the effecting the condensation of the steam, not in the cylinder itself, which was thereby greatly cooled, and occasioned the waste of much steam in being heated again at every stroke, but in a separate air-tight vessel, called the condenser, which is kept cool and vacuous. Into this condenser, the steam is allowed to escape from above and from below the piston alternately, and a vacuum is obtained without ever reducing the temperature of the cylinder below 212° .

A third and more recent improvement in the employment of steam as a moving power, consists in using it *expansively*, a mode of application which will be best understood by being explained in a particular case. Let it be supposed that a piston loaded with one ton, is raised four feet by filling the cylinder in which it moves with low-pressure steam, or steam of the tension of one atmosphere. An equivalent effect may be produced at the same expense of steam, by filling one fourth of the cylinder with steam of the tension of four atmospheres, and loading the piston with four tons, which will be raised one foot. But the piston being raised one foot by steam of four atmospheres, and in the position represented in the figure, the



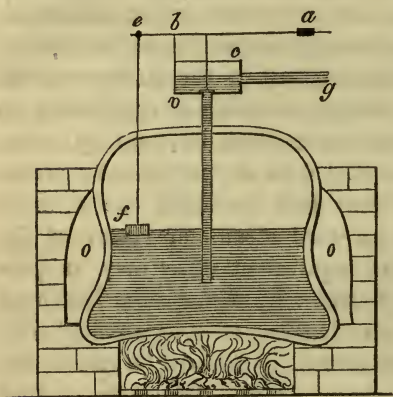
supply of steam may be cut off, and the piston will continue to be elevated in the cylinder by the simple expansion of the steam below it, although with a diminishing force. When the piston has been raised another foot in the cylinder, or two feet from the bottom, the volume of the steam will be doubled, and its tension consequently reduced from four to $\frac{2}{3}$, or two atmospheres. At a height of three feet in the cylinder, the piston will have steam

below it of the tension of $\frac{1}{4}$ or $1\frac{1}{3}$ atmosphere, and when the

piston is elevated four feet, or reaches the top of the cylinder, the tension of the steam below it will still be $\frac{1}{4}$ or one atmosphere. The piston has, therefore, been raised to a height of three feet, with a force progressively diminishing from four atmospheres to one, or with an average force of two atmospheres, by means of a power acquired without any consumption of steam, but by the expansion merely of steam that had already produced its usual effect.

The boiler used to produce the steam is constructed of different forms. The common *wagon* boiler is represented in Figure 1. The heated air from the fire below the boiler, after passing under its whole length, is brought back, before passing

FIG. 1.



to the chimney, by flues, *o, o*, in order that what heat the air still contains, may be imparted to the sides of the boiler. The water is supplied in proper quantity to the boiler, and kept at a constant level from a fountain-head *g*, by a tube descending into the boiler from a box above it *c v*. The mouth of this tube is closed by a valve, which is kept shut by pressure from the lever *a b*, loaded at *a*. But to the other limb *b e* of the lever an iron-rod is attached, which descends into the boiler, and is fixed to a piece of wood *f*, which floats upon the surface of the water. When the level of the water is lowered, *f* falls with it, and occasions the valve above to be opened and water to flow into the boiler.

FIG. 2.

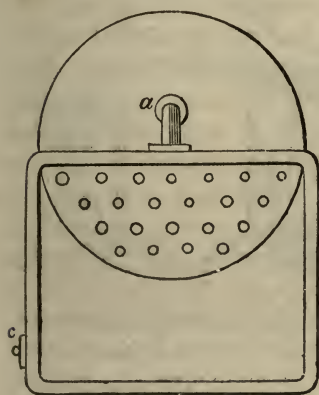


The cylinder boiler, of which a section is given in Figure 2, is preferred as the most economical, for the great steam-engines at the Cornish mines. It consists of two cylinders, one within the other, the smaller cylinder containing the fire, and the space between the two cylinders being occupied by the water. The

outer cylinder may be six feet in diameter, and is often fifty or sixty feet in length. The heated air from the fire, after traversing the inner cylinder is conducted under the boiler by the flues *o, o*, before it is conveyed to the chimney.

In locomotive steam-engines, where the principal object is to generate steam in a small and compact apparatus with great rapidity, a different construction is adopted. Here the boiler

FIG. 3.

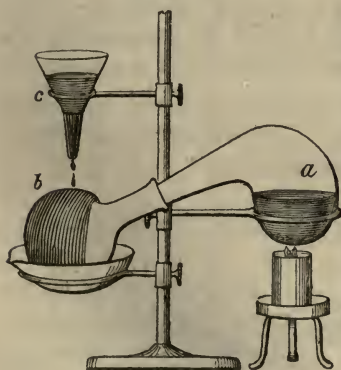


consists of two parts, a square box with a double casing, of which a section is given in Figure 3, which contains the fire, surrounded by water in the space between the casings; and a cylinder *a*, through the lower part of which pass a number of copper tubes of small size, which communicate at one end with the fire-box, and at the other with the chimney, and form a passage for the heated air from the fire to the chimney. By means of these tubes, the object is accomplished of exposing to a source of heat, the greatest

possible quantity of surface in contact with the water.—(See *Dr. Lardner on the Steam-Engine, Cabinet Cyclopaedia*).

The subject of distillation is a natural sequel to vaporization; but it is unnecessary to enter into much detail. The principal point to be attended to is the most efficient mode of condensing the vapour. Figure 1. represents the ordinary arrangement in

FIG. 1.

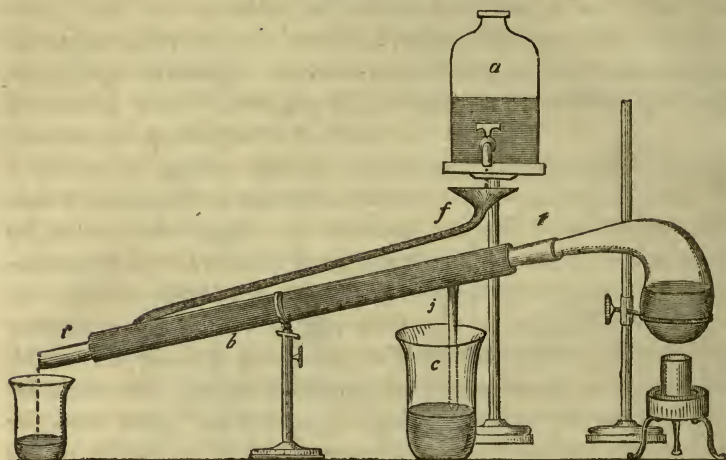


distilling a liquid from a retort *a*, and condensing the vapour in a glass flask *b*, which is kept cool by water dropping upon it from a funnel above *c*. The condensing flask is covered by bibulous paper, so that the water falling upon it may be made to pass equably over its surface, and it is supported in a basin likewise containing cold water.

But a much superior instrument to the condensing flask is

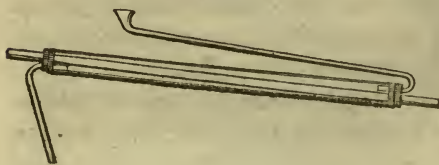
the condensing tube of Professor Liebig, (Figure 2). This is a plain glass tube, *t t* about eighteen inches in length, and two-

FIG. 2.



thirds of an inch internal diameter, which is enclosed in a larger tube *b*, of brass or tin-plate, about twelve inches long and two inches in diameter, the ends of which are closed by perforated corks. A constant supply of cold condensing water from a vessel *a* is introduced into the space between the two tubes, being conveyed to the lower part of the instrument by the funnel and tube *f*, and flowing out from the upper part by the tube *g*. The condensed liquid drops quite cool from the lower extremity of the glass tube, where a vessel is placed to receive it. This is an admirable apparatus, and ought to supersede all other means of condensation in the laboratory. The spiral copper tube or worm which is used for condensing in the common still, is commonly made longer than is necessary, and from its form cannot be examined and cleaned like a straight tube. Much vapour may be condensed by a small extent of surface, provided it is kept cold by an ample supply of condensing water.

FIG. 3.

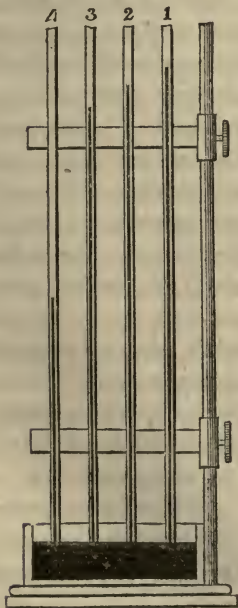


Both the outer and inner tube may be of glass in the condensing apparatus which has been described, and then the small tubes to bring and

carry off the condensing water, may be made to pass through openings in the corks, which they fit, as represented in Figure 3.

Evaporation in vacuo. Water rises rapidly into vapour in a vacuous space, without the appearance of ebullition, at all temperatures, even at 32° , and greatly lower. Its elastic force increases as the temperature is elevated, till at 212° , it is equal to that of the atmosphere, or capable of supporting a column of mercury thirty inches in height. Various other solid and liquid substances emit vapour in similar circumstances, such as camphor, alcohol, ether, and oil of turpentine. Such bodies are said to be *volatile*, and other bodies, such as marble, the metals, &c. which do not emit a sensible vapour at the temperature of the air, are said to be *fixed*. All bodies which boil at low temperatures belong to the volatile class. An accurate estimate of the volatility of different bodies is obtained by determining the elastic force of the vapour which they emit in the vacuous space above the column of mercury of the barometer. If we pass up a bubble of air into the vacuum of the barometer, above the mercurial column, standing at the time at a height of 30 inches, the mercury is depressed, we may suppose to the level of 29 inches, or by one inch. This would indicate that the air, by

rising above the mercury, has been expanded into thirty times its former bulk, or that the elastic force of this rare air is equal to a column of one inch of mercury. The elastic force of vapour is estimated in the same manner. A few drops of the liquid operated upon are passed up into the vacuum above the mercurial column, which is depressed in proportion to the elastic force of the vapour. The depression produced by various liquids is very different, as illustrated in the annexed figure, representing four barometer tubes, in which the mercury is at its proper height in No. 1; is depressed by the vapour of water of the temperature 60° in No. 2; and by alcohol and ether at the same temperature in Nos. 3 and 4 respectively.



The depression of the mercurial column produced by water at every degree of temperature, between 32° and 212° , was carefully determined by Dr. Dalton, and his results have been confirmed by Dr. Ure. The following selected observations prove that the elasticity increases at a very rapid rate with the temperature.

Tension of the vapour of water in inches of mercury.				Temperature.
0.2	inch at	.	.	32°
0.263	"	.	.	40
0.375	"	.	.	50
0.524	"	.	.	60
0.721	"	.	.	70
1	"	.	.	80
1.36	"	.	.	90
1.86	"	.	.	100
7.42	"	.	.	150
23.64	"	.	.	200
30	"	.	.	212

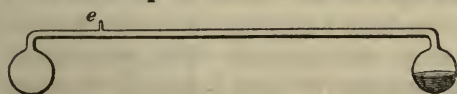
The vapours of other liquids increase in density and elastic force with the temperature, as well as the vapour of water; but each vapour appears to follow a rate of progression peculiar to itself.

The assumption of latent heat by such vapours is evinced in some processes for producing cold. Water may be frozen by the evaporation of ether in the air-pump, and a cold produced of 55 degrees under the zero of Fahrenheit by the evaporation of that fluid. The ether-vapour derives its store of latent heat from the remaining fluid, and contiguous bodies, which are robbed of their heat, and suffer a great refrigeration. To sustain the evaporation of this fluid, it is necessary to withdraw the vapour as it is produced by continual pumping. The volatile liquid, sulphuret of carbon, substituted for ether, produces even greater effects.

On the same principle is founded Leslie's elegant process for the freezing of water by its own evaporation, within the exhausted receiver of an air-pump, the evaporation being kept up by the absorbent power of sulphuric acid. A little water, in a cup of porous stone-ware, is supported over a shallow basin containing sulphuric acid. All that is necessary is to produce a good exhaustion at first: the process of evaporation and absorption then go on spontaneously, in an uninter-

rupted manner. Various bodies, which have a powerful attraction for watery vapour, may be used as absorbents, such as parched oatmeal, the powder of mouldering whinstone, and even dry sole-leather, by means of any one of which a small quantity of water may be frozen, during summer, in the exhausted receiver of an air-pump. No substance, however, is superior, in this respect to concentrated sulphuric acid. When this liquid becomes too dilute to act powerfully as an absorbent, it may be rendered again fit for use, by boiling it and driving off the water. Ice might be procured in quantity, in a warm climate, by this process. The necessary vacuum would be most easily commanded, on the large scale, by allowing the receivers to communicate with a strong drum, filled with steam, which could be condensed.

In the *Cryophorus* of Dr. Wollaston, water is also frozen by its own evaporation. This instrument consists of two glass



bulbs, connected by a tube, and containing a portion of water, as represented in the figure.

The air is first entirely expelled from the instrument by boiling the water, in both bulbs, at the same time, and allowing the steam to escape by a small opening at the extremity of the little projecting tube *e*. While the instrument is entirely filled with steam, the point of *e* is fused by the blow-pipe flame, and the opening hermetically closed. In experimenting with this instrument, the water is all poured into one bulb, and the other or empty bulb placed in a basin containing a freezing mixture of ice and salt. The vapour in the cooled bulb is condensed, but its place is supplied by vapour from the water in the other bulb. A rapid evaporation takes place in the water bulb, and condensation in the empty bulb, till the water in the former bulb is cooled so low as to freeze. The instrument derives its name of the *cryophorus*, or frost-bearer, from this transference of the cold of the bulb in the freezing mixture to the bulb at a distance from it.

It is by the evaporation of liquefied carbonic acid, that Thilorier produces the extreme depression of temperature, -135° , which he has attained and measured. He allows a small stream of liquid carbonic acid to escape, from a magazine of the liquid, into a cylindrical box of wood, like a round snuff box in shape. The stream of liquid, which immediately becomes in part gas, is made, as it enters the box, to strike against a plain surface at

such an inclination as to cause the gas to circulate round the circumference of the cavity of the box, instead of traversing it in a straight line. The box is speedily filled with a light powder, having the appearance of snow, which is solid carbonic acid, one portion of the liquid carbonic acid being frozen by the evaporation of the other. The solid carbonic acid is an imperfect conductor of heat, and is on that account not immediately dissipated by evaporation. It is most conveniently applied as a frigorific agent when mixed with ether, with which it forms a soft mass, like half-melted snow. Mercury may be frozen in large quantity, by throwing a portion of this compound upon the surface of the fluid metal. The ether evaporates as well as the carbonic acid, and contributes to produce the cold. To form the liquid carbonic acid itself in large quantity, M. Thilorier makes use of two strong cylindrical vessels of wrought iron, like mercury bottles in size and form, one of which is called the generator, and the other the receiver. The generator is lined with lead, and is intended for the reception of strong muriatic acid and marble, the materials for the production of the gas. It is connected with the receiver by a short iron pipe, which is provided with a stop-cock, so that the receiver can be separated from the generator, without loss of gas from the former. The generator is charged with materials several times in succession, and the product accumulated in the receiver till it may amount to a pound or two. The stop-cock and screws in this apparatus must be of the most accurate workmanship, and be screwed down upon leaden washers.

The question arises, do those bodies which evaporate at a moderate temperature continue to evaporate at all temperatures, however low? The opinion has prevailed, that bodies which are decidedly vaporous at high temperatures, such as sulphuric acid and mercury, never cease to evolve vapour, however far their temperature may be depressed, although the quantity emitted becomes less and less, till it ceases to be appreciable by our senses. Even fixed bodies, such as metals, rocks, &c., have been supposed to allow an escape of their substance into air at the ordinary temperature; and hence the atmosphere has been supposed to contain traces of the vapours of all the bodies with which it is in contact. Certain researches of Dr. Faraday, published in the Philosophical Transactions for 1826, on the existence of a limit to vaporiza-

tion, established the opposite conclusion. Mercury was found to yield a small quantity of vapour during summer, at a temperature varying from 60° to 80° , but in winter no trace of vapour could be detected. Dr. Faraday has proved that several chemical agents, which may be volatilized by a heat between 300° and 400° , did not undergo the slightest evaporation when kept in a confined space with water during four years.

Bodies, therefore, cease all at once to emit vapour, at some particular temperature. In the case of mercury, this temperature lies between 40° and 60° Fahrenheit. But a progressive and endless diminution of vaporizing power is certainly more natural than an abrupt cessation. What puts a stop to vaporization? it may be asked. Liquids, we know, have a certain attraction for their own particles, evinced in their disposition to collect together in drops. The particles of solids are attracted more powerfully, and cohere strongly together. Dr. Faraday is of opinion, that when the vaporizing power becomes very weak, at low temperatures, it may be overcome and negatived completely by this cohesive attraction, and no escape of particles in the vaporous form be permitted.

This supposition is conformable with the views of corpuscular philosophy entertained by Laplace. According to that profound philosopher, the form of aggregation which a body affects depends upon the mutual relation of three forces : 1. The attraction of each particle for the other particles which surround it, which induces them to approach as near as possible to each other. 2. The attraction of each particle for the heat which surrounds the other particles in its neighbourhood. 3. The repulsion between the heat which surrounds each particle, and that which surrounds the neighbouring particles, a force which tends to disunite the particles of bodies. When the first of these forces prevails, the body is solid ; if the quantity of heat augments, the second force becomes dominant, the particles then move among each other with facility, and the body is liquid. While this is the case, the particles are still retained by the attraction for the neighbouring heat, within the limits of the space which the body formerly occupied, except at the surface, where the heat separates them, that is to say, occasions evaporation, till the influence of some pressure prevents the separation from being effected. When the heat increases to such a degree that the reciprocal repulsive force

prevails over the attraction of the particles for one another, they disperse in all directions, as long as they meet no obstacle, and the body assumes the gaseous form. Berzelius adds the reflection, that if, in that gaseous state, into which Cagnard de la Tour reduced some volatile liquids, the pressure does not correspond with the result of calculation, that difference may depend on this: that, as the particles have not an opportunity to recede much, the two first forces continue always to act, and oppose the tension of the gas, which does not establish itself in all its power unless when the particles are so distant from each other as to be out of the sphere of the influence of these forces.*

Gases. Permanent gases, such as atmospheric air, unquestionably owe their elastic state to the possession of latent heat. But the theory of the similar constitution of gases and vapours, although supported by strong analogies, was not generally adopted by chemists, till it was experimentally confirmed by Dr. Faraday, who liquefied several of the gases.† His method was to generate the gas in one end of a strong glass tube, bent

in the middle, as represented in the figure, and hermetically sealed. The gas accumu-

lating in a confined space, comes to exert a prodigious pressure, an effect of which is, that a portion of the gas itself condenses into a liquid in the end of the tube most remote from the materials, which is kept cool with that view. Considerable danger is to be apprehended by the operator in conducting such experiments, from the bursting of the glass tubes, and the face ought always to be protected by a wire-gauze mask from the effects of an explosion. The names of the gases which were liquefied in this manner, are sulphurous acid, cyanogen, chlorine, ammoniacal gas, sulphuretted hydrogen, carbonic acid, muriatic acid, and nitrous oxide; which required a degree of pressure varying, in the different gases, from two atmospheres, in the first mentioned, to fifty atmospheres, in the last mentioned gas, at the temperature of 45°. The liquefaction of several of these gases

* *Traité de Chimie*, par J. J. Berzelius, t. 1, p. 85.

† *Philosophical Transactions*, 1823, p. 189.

has since been effected by the application of cold alone, without compression.

The elastic force of the vapours arising from these gases increases at a rapid rate with their temperature. Thus the vapour from liquefied ammonia at 32° was found to exert a pressure of 5 atmospheres, and when heated to 52° , a pressure of $6\frac{1}{2}$ atmospheres; the vapour from liquid sulphuretted hydrogen at 3° exerted a pressure of 14 atmospheres, and at 47° a pressure of 17 atmospheres. Liquid muriatic acid at 32° , 22° , and 47° respectively, exerted a force of 20, 25, and 40 atmospheres; carbonic acid at 12° and 32° , a force of 20 and 36 atmospheres. Sir H. Davy threw out the idea that the prodigious elastic force of these fluids might be used as a moving power. But supposing the application practicable, it may be doubted, from what we know of the constancy of the united sum of the latent and sensible heat of high pressure steam, whether any saving of heat would be effected by such an application of the vapours of the liquefied gases.

In certain gases, particularly hydrogen, nitrogen, oxygen, nitric oxide, and carburetted hydrogen, compression alone seems inadequate to produce liquefaction; for these gases have preserved their elastic form under a pressure of at least 800 atmospheres. There can be little doubt, however, that all other gases at present known would yield to a less compressing force. Exposure to extreme cold, with the application of great pressure at the same time, is the most likely means of liquefying the more refractory gases.

All gases whatever are absorbed and condensed by water in a greater or less degree, in which case they certainly assume the liquid form. The quantity condensed is widely different in the different gases; and in the same gas the quantity condensed depends upon the pressure to which the gas is subjected, and the temperature of the absorbing water. In the case of carbonic acid gas, Dr. Henry proved that the *volume* absorbed by water is the same, whatever be the pressure to which the gas is subject. Hence, we double the weight or quantity of gas absorbed by subjecting it, in contact with water, to the pressure of two atmospheres; and this practice is adopted in impregnating water with carbonic acid, to make soda-water. The colder the water, the greater also the quantity of gas absorbed.

In the physical theory of gases, they are assumed to be ex-

pansible to an indefinite extent, in the proportion that pressure upon them is diminished, and to be contractible under increased pressure exactly in proportion to the compressing force—the well-known law of Mariotte. The bulk of atmospheric air has been found rigidly to correspond with this law, when it was expanded into 300 volumes, and also when compressed into 1-25th of its primary volume. But there is reason to doubt whether the law holds with absolute accuracy, in the case of a gas either in a state of extreme rarefaction, or of the greatest density. Thus atmospheric air does not appear to be indefinitely expansible; for there is certainly a limit to the earth's gaseous atmosphere, and it does not expand into all space. Dr. Wollaston supposed that the material particles of air are not indefinitely minute, but have a certain magnitude and weight. These particles are under the influence of a powerful mutual repulsion, as is always the case in gaseous bodies, and, therefore, tend to separate from each other; but as this repulsive force diminishes as the distance of the particles from each other increases, Dr. Wollaston imagined that the weight of the individual particles might come at last to balance it, and thus prevent their farther divergence. On this view, which is exceedingly probable, the expansion of a gas, caused by the removal of pressure, will cease at a particular stage of rarefaction, and the gas not expanding farther, will come to have an upper surface, like a liquid. The earth's atmosphere has probably an exact limit, and true surface.

The deviation from the law of Mariotte, in the case of gases under a greater pressure than that of the atmosphere, has been distinctly observed in the more liquefiable gases. Thus, Professor Oersted, of Copenhagen, found that sulphurous acid gas diminishes, under increased pressure, more rapidly than common air. The volumes of atmospheric air and of the gas were equal at the following pressures:

Pressure upon air in atmospheres.		Pressure upon sulphurous gas in atmospheres.
1	.	1
1.175	.	1.173
2.821	.	2.782
3.319	.	3.189

It will be observed that less pressure always suffices to reduce the sulphurous acid gas to the same bulk than is required by

air. If the pressure upon the air and gas were made equal, then the gas would be compressed into less bulk than the air, and deviate from the law of Mariotte. Despretz has more lately observed an equally conspicuous deviation from this law under increasing pressures, in several other gases, particularly sulphuretted hydrogen, cyanogen, and ammonia, which are all easily liquefied. There is no reason, however, to suppose that any partial liquefaction of the gases occurs under the pressure applied to them in such experiments. They remain entirely gaseous, and their superior compressibility, must be referred to a law of their constitution. It is the phenomenon beginning to show itself in a gas under moderate pressure, which was observed in all its excess by Cagnard de la Tour, in the vapours confined by him under great pressure, (page 53.)

Those gases, which exhibit this deviation, must occupy less bulk than they ought to do under the pressure of the atmosphere itself; which may be the reason why the liquefiable gases are generally found by experiment to be specifically heavier than they ought by theory to be.

Such are the most remarkable features which gases exhibit in relation to pressure and temperature. These properties are independent of the specific weights of the gases, which are very different in the various members of the class, and they are but little connected with the nature of the particular substance or material which exists in the gaseous form. But when different gases are presented to each other, a new property of the gaseous state is developed, namely the forcible disposition of different gases to intermix, or to diffuse themselves through each other. This is a property which interferes in a great variety of phenomena, and is no less characteristic of the gaseous state than any we have considered. It may be treated of under the head, 1° of the diffusion of gases through each other, and 2° of the diffusion of vapours into gases, by which is meant, the ascent of vapours from volatile bodies into air and other gases, of which the spontaneous evaporation of water into the air is an instance.

Diffusion of gases. When a light and heavy gas are once mixed together, they do not exhibit any tendency to separate again, on standing at rest for some time, differing in this respect from mixed liquids, many of which speedily separate, and arrange themselves according to their densities,

the lightest uppermost, and the heaviest undermost, as in the familiar example of oil and water, unless they have combined together. This peculiar property of gases has repeatedly been made the subject of careful experiment. Common air, for instance, is essentially a mixture of two gases, differing in weight in the proportion of 976 to 1103, but the air in a tall close tube of glass several feet in length, kept upright in a still place, has been found sensibly the same in composition at the top and bottom of the tube, after a lapse of months. Hence, there is no reason to imagine that the upper strata of the air differ in composition from the lower; or that a light gas, such as hydrogen, escaping into the atmosphere will rise, and ultimately possess the higher regions; suppositions which have been made the groundwork of meteorological theories at different times.

The earliest observations we possess on this subject are those of Dr. Priestley, to whom pneumatic chemistry stands so much indebted. Having repeated occasion to transmit a gas through stoneware tubes surrounded by burning fuel, he perceived that the tubes were porous, and that the gas escaped outwards into the fire, while at the same time the gases of the fire penetrated into the tube, although the gas within the tube was in a compressed state.

Dr. Dalton, however, first perceived the important bearings of this property of aerial bodies, and made it the subject of experimental inquiry. He discovered that any two gases, allowed to communicate with each other, exhibit a positive tendency to mix or to penetrate through each other, even in opposition to the influence of their weight. Thus, a vessel containing a light gas (hydrogen,) being placed above a vessel containing a heavy gas (carbonic acid,) and the two gases allowed to communicate by a narrow tube, as represented in the figure, an interchange speedily took place of a portion of their contents, which it might have been supposed that their relative position would have prevented. Contrary to the solicitation of gravity, the heavy gas continued spontaneously to ascend and the light gas to descend, till in a few hours they became perfectly mixed, and the proportion of the two gases was the same in the upper and lower vessels. This disposition of different gases to intermix, appeared to Dr. Dalton so decided and strong, as to justify



the inference that different gases afford no resistance to each other; but that one gas spreads or expands into the space occupied by another gas, as it would rush into a vacuum. At least, that the resistance which the particles of one gas offer to those of another is of a very imperfect kind, to be compared to the resistance which stones in the channel of a stream oppose to the flow of running water. Such is Dr. Dalton's theory of the miscibility of the gases. (Manchester Memoirs, vol. 5.)

In entering into this inquiry I found, first, that gases diffuse into the atmosphere and into each other, with different degrees of ease and rapidity. This was observed by allowing each gas to diffuse from a bottle into the air through a narrow tube, taking care, when the gas was lighter than air, that it was allowed to escape from the lower part of the vessel, and when heavier from the upper part, so that it had, on no occasion, any disposition to flow out, but was constrained to diffuse in opposition to the effect of gravity. The result was, that the same quantity of different gases escapes in times which are exceedingly unequal, but have a relation to the specific gravity of the gas. The light gases diffuse or escape most rapidly; thus, hydrogen escapes five times quicker than carbonic acid, which is twenty-two times heavier than that gas. Secondly, in the case of an intimate mixture of two gases, the most diffusive gas separates from the other, and leaves the receiver in the greatest proportion. Hence, by availing ourselves of the tendencies of mixed gases to diffuse with different degrees of rapidity, a sort of mechanical separation of gases may be effected. The mixture must be allowed to diffuse for a certain time into a confined gaseous or vaporous atmosphere, of such a kind as may afterwards be condensed or absorbed with facility.*

But the nature of the process of diffusion is best illustrated when the gases communicate with each other through minute pores or apertures of insensible magnitude.

A singular observation belonging to this subject was made by Professor Dobereiner of Jena, on the escape of hydrogen gas by a fissure or crack in glass receivers. Having occasion to collect large quantities of that light gas, he had accidentally

* Quarterly Journal of Science. New Series, Vol. V.

made use of a jar which had a slight fissure in it. He was surprised to find that the water of the pneumatic trough rose into this jar, one and a half inches in 12 hours; and that after 24 hours, the height of the water was two inches two thirds above the level of that in the trough. During the experiment, neither the height of the barometer, nor the temperature of the place had sensibly altered.* He ascribed the phenomenon to capillary action, and supposed that hydrogen only is attracted by the fissures, and escapes through them on account of the extreme smallness of its atoms. It is unnecessary to examine this explanation, as Dobereiner did not observe the whole phenomenon. On repeating the experiment, and varying the circumstances, it appeared to me that hydrogen never escapes outwards by the fissure without a certain portion of air penetrating at the same time inwards, amounting to between one-fourth and one-fifth of the volume of the hydrogen which leaves the receiver. It was found by an instrument, which admits of much greater precision than the fissured jar, that when hydrogen gas communicates with air through such a chink, the air and hydrogen exhibit a powerful disposition to exchange places with each other; a particle of air, however, does not exchange with a particle of hydrogen of the same magnitude, but of 3.83 times its magnitude. We may adopt the word *diffusion-volume*, to express this diversity of disposition in gases to interchange particles, and say that the diffusion-volume of air being 1, that of hydrogen gas is 3.83. Now every gas has a diffusion-volume peculiar to itself, and depending upon its specific gravity. Of those gases which are lighter than air, the diffusion-volume is greater than 1, and of those which are heavier, the diffusion-volume is less than 1.†

Exact results are obtained by means of a simple instrument, which may be called a diffusion tube, and which is constructed as follows. A glass tube, open at both ends, is selected, half an inch in diameter, and from six to fourteen inches in length. A cylinder of wood, somewhat less in diameter, is in-

* Annales de Chimie et de Physique, 1825.

† The mathematical relation which subsists between the diffusion-volume, and the density of a gas is expressed thus :

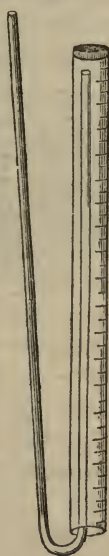
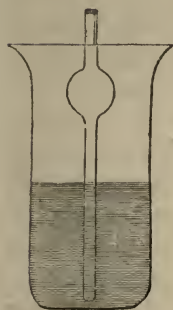
$$\text{Diffusion-volume} = \frac{1}{d^{\frac{1}{2}}}$$

where d represents the specific gravity of the gas.

troduced into the tube, so as to occupy the whole of it, with the exception of about one-fifth of an inch at one extremity, which space is filled with a paste of Paris plaster, of the usual consistence for casts. In the course of a few minutes the plaster sets, and on withdrawing the wooden cylinder, the tube forms a receiver, closed by an immoveable plate of stucco. In the wet state, the stucco is air-tight; it is therefore dried, either by exposure to the air for a day, or by placing it in a temperature of 200° for a few hours; and is thereafter found to be permeable by gases, even in the most humid atmosphere, if not positively wetted. When such a diffusion-tube, six inches in length, is filled with hydrogen over mercury,

FIG. 2.

FIG. 1.



the diffusion, or exchange of air for hydrogen, instantly commences through the minute pores of the stucco, and proceeds with so much force and velocity, that within three minutes, the mercury attains a height in the receiver of more than two inches above its level in the trough; within twenty minutes, the whole of the hydrogen has escaped. In conducting such experiments over water, it is necessary to avoid wetting the stucco. With this view, before filling the diffusion tube with hydrogen, the air is withdrawn by placing the tube upon the short limb of an empty syphon, (see Figure 1), which does

not reach, but comes within half an inch of the stucco, and then sinking the instrument in the water trough, so that the air escapes by the syphon, with the exception of a small quantity, which is noted. The diffusion tube is then filled up, either entirely or to a certain extent, with the gas to be diffused.

The ascent of the water in the tube, when hydrogen is diffused, forms a striking experiment. But in experiments made with the purpose of determining the proportion between the gas diffused and the air which replaces it, it is necessary to guard against any inequality of pressure, by placing the diffusion tube

in a jar of water as in Figure 2, and filling the jar with water in proportion as it rises in the tube.*

In this instrument we may substitute many other porous substances for the stucco; but few of them answer so well. Dry and sound cork is very suitable, but permits the diffusion to go on very slowly, not being sufficiently porous; so do thin slips of many granular foliated minerals, such as flexible magnesian limestone. Charcoal, woods, unglazed earthenware, dry bladder, may all be used for the same purpose.

A slight deviation from the law is observed in gases which differ in a certain physical property from air, namely, in the greater facility with which they may be forced through pores or minute apertures by pressure. A dissimilarity between the gases, in this respect, had long been recognized, although no accurate experiments had been made on the subject. It became, however, necessary to examine this point. A small bell-jar, with a short neck and opening at the top, was used, which opening was closed by a plate of stucco half an inch in thickness, over which a brass cap and stopcock were fitted and cemented. This receiver was placed on the plate of an air-pump in perfect order, and exhausted. When the stopcock was closed, nothing entered the exhausted receiver; but on opening it, either air entered, forcing its way through the pores of the stucco, or any gas which might be conducted to it, by means of a flexible tube from a proper magazine. Gas was allowed to enter, till it acquired a pressure of three inches, always setting out with air of the tension of one inch mercury in the receiver.

The same quantity of different gases entered in the following times :

Air, dry	in 10'
Air, saturated with moisture, at 60°					10'
Carbonic acid	10'
Nitrogen	10'
Oxygen	10'

* A diffusion experiment affords the elements for calculating the specific gravity of a gas.

$$\text{The specific gravity} = \left(\frac{A}{G}\right)^2$$

where G is the measure of gas submitted to diffusion, and A the measure of return air.—Edinb. Phil. Trans. XII, 222; or Phil. Mag. 3rd series, II, 175.

Carbonic oxide	.	.	.	9' 30"
Olefiant gas	.	.	.	7' 50"
Coal gas	.	.	.	7'
Hydrogen	.	.	.	4'

Hydrogen, therefore, entered under pressure 2.4 times, or nearly $2\frac{1}{2}$ times quicker than air, while several gases had the same rate as air. Those gases which percolate very easily, enter the diffusion instrument somewhat in excess, particularly when the plate of stucco is thin. The deviation is perceptible in hydrogen, and olefiant gas, and is also very sensible in coal gas and carburetted hydrogen.

It can be shown, on the principles of pneumatics, that gases should rush into a vacuum with velocities corresponding to the numbers which have been found to express their diffusion volumes; that is, with velocities inversely proportional to the square root of the densities of the gases. The law of the diffusion of gases has on this account been viewed by my friend, Mr. T. S. Thomson, of Clitheroe, as a confirmation of Dr. Dalton's theory, that gases are inelastic towards each other.* It must be admitted that the ultimate result in diffusion is in strict accordance with Dalton's law, but there are certain circumstances which make me hesitate in adopting it as a true representation of the phenomenon, although it affords a convenient mode of expressing it. 1. It is supposed, on that law, that when a cubic foot of hydrogen gas is allowed to communicate with a cubic foot of air, the hydrogen *expands* into the space occupied by the air, as it would do into a vacuum, and becomes two cubic feet of hydrogen of half density. The air, on the other hand, expands in the same manner into the space occupied by the hydrogen, so as to become two cubic feet of air of half density. Now if the gases actually expanded through each other in this manner, cold should be produced, and the temperature of the mixed gases should fall 40 or 45 degrees. But not the slightest change of temperature occurs in diffusion, however rapidly the process is conducted. 2. Although the ultimate result of diffusion is always in conformity with Dalton's law, yet the diffusive process takes place in different gases with very different degrees of rapidity. Thus, the external air penetrates

* Phil. Mag. 3rd series, IV, 321.

into a diffusion tube with velocities denoted by the following numbers, 1277, 623, 302, according as the diffusion tube is filled with hydrogen, with carbonic acid, or with chlorine gas. Now, if the air were rushing into a vacuum in all these cases, why should it not always enter it with the same velocity? Something more, therefore, must be assumed than that gases are vacua to each other, in order to explain the whole phenomena observed in diffusion.

Passage of gases through membranes. In connexion with diffusion, the passage of gases through humid membranes may be noticed. If a bladder, half filled with air, with its mouth tied, be passed up into a large jar filled with carbonic acid gas, standing over water, the bladder, in the course of twenty-four hours becomes greatly distended, by the insinuation of the carbonic acid through its substance, and may even burst, while a very little air escapes outwards from the bladder. But this is not simple diffusion. The result depends upon two circumstances; first, upon carbonic acid being a gas easily liquefied by the water in the substance of the membrane,—the carbonic acid penetrates the membrane as a liquid; secondly, this liquid is in the highest degree volatile, and, therefore, evaporates very rapidly from the inner surface of the bladder into the air confined in it. The air in the bladder comes to be expanded in the same manner as if ether or any other volatile fluid was admitted into it. The phenomenon was observed by Dalton in its simplest form. Into a very narrow jar, half filled with carbonic acid gas over water, he admitted a little air. The air and gas were accidentally separated by a water bubble, and thus prevented from intermixing. But the carbonic gas immediately began to be liquefied by the film of water, and passing through it, evaporated into the air below. The air was in this way gradually expanded, and the water bubble ascended in the tube. Here the particular phenomenon in question was observed to take place, but without the intervention of membrane. It is to be remembered that the thinnest film of water or any liquid is absolutely impermeable to a gas as such.

In the experiments of Drs. Mitchell and Faust and others, in which gases passed through a sheet of caoutchouc, it is to be supposed that the gases were always liquefied in that substance, and penetrated through it in a fluid form. Indeed few bodies are more remarkable than caoutchouc for the avidity with which

they imbibe various liquids. The absorption of ether, of naphtha, of oil of turpentine, which soften the substance of the caoutchouc, without dissolving it, may be referred to. It is likewise always those gases which are more easily liquefied by cold or pressure that pass most readily through both caoutchouc and humid membranes. Dr. Mitchell found that the time required for the passage of equal volumes of different gases, through the same membrane, was

1	minute,	with ammonia.
$2\frac{1}{2}$	minutes,	with sulphuretted hydrogen.
$3\frac{1}{4}$	„	cyanogen.
$5\frac{1}{2}$	„	carbonic acid.
$6\frac{1}{2}$	„	nitrous oxide.
$27\frac{1}{2}$	„	arsenietted hydrogen.
28	„	olefiant gas.
$37\frac{1}{2}$	„	hydrogen.
113	„	oxygen.
160	„	carbonic oxide,

and a much greater time with nitrogen.

Diffusion of Vapours into air, or spontaneous evaporation. Volatile bodies, such as water, rise into air as well as into a vacuum, and obviously according to the law, by which gases diffuse through each other. Thus if a small quantity of the volatile liquid ether be conveyed into two tall jars standing over water, one half filled with air, and the other with hydrogen gas, the air and hydrogen immediately begin to expand, from the ascent of the ether-vapour into them, and the two gases in the end have their volume increased exactly in the same proportion. But the hydrogen gas undergoes this expansion in half the time that the air requires; that is to say, ether-vapour follows the usual law of diffusion in penetrating more rapidly through the lighter gas.

We are indebted to Dr. Dalton for the discovery that the evaporation of water has the same limit in air as in a vacuum. Indeed the quantity of vapour from a volatile body which can rise into a confined space, is exactly the same, whether that space be a vacuum, or already filled with any air or gas, in any state of rarefaction or condensation. The vapour rises and adds its own elastic force, such as it exhibits in a vacuum, to the elastic force of the other gases or vapours already occupying the same space. Hence, it is only necessary to know what

quantity of any vapour rises into a vacuum at any particular temperature ;—the same quantity rises into air. Thus the vapour from water, which rises into a vacuum at 80° , depresses the mercurial column one inch, or its tension is one thirtieth of the usual tension of the air. Now, if water at 80° be admitted into dry air, it will increase the tension of that air by 1—30th, if the air be confined; or increase its bulk by 1—30th if the air be allowed to expand.

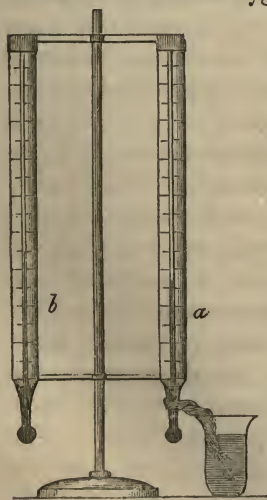
The spontaneous evaporation of water into air is much affected by three circumstances: 1^o. the previous state of dryness of the air, for a certain fixed quantity only of vapour can rise into air, as much as into the same space if vacuum; and if a portion of that quantity be already present so much the less will be taken up by the air; and no evaporation whatever takes place into air which contains this fixed quantity, and is already saturated with humidity. 2^o. By warmth, for the higher the temperature the more considerable is the quantity of vapour which rises into any accessible space. Thus water emits so much vapour at 40° as expands the air in contact with it 1—114th part, and at 60° as much as expands air 1—57th part, or double the quantity emitted at the lower temperature. Hence, humid hot air contains a much greater portion of moisture than humid cold air. 3^o. The evaporation of water is greatly quickened by the removal of the incumbent air in proportion as it becomes saturated; and hence a current of air is exceedingly favourable to evaporation.

When air saturated with humidity at a high temperature is cooled, it ceases to be able to sustain the large portion of vapour which it possesses, and the excess assumes the liquid form, and precipitates in drops. Many familiar appearances depend upon the condensation of the vapour in the atmosphere. When a glass of cold water, for instance, is brought into a warm room, it is often quickly covered with moisture. The air in contact with the glass is chilled, and its power to retain vapour so much reduced as to occasion it to deposit a portion upon the cold glass. It is from the same cause that water is often seen in the morning running down in streams upon the inside of the glass panes of bed-room windows. The glass has the low temperature of the external air, and by contact cools the warm and humid air of the apartment so as to occasion the precipitation of its moisture. Hence also, when a warm thaw follows

after frost, thick stone walls which continue to retain their low temperature, are covered by a profusion of moisture.

Hygrometers. As water evaporates at all temperatures, however low, the atmosphere cannot be supposed to be ever entirely destitute of moisture. The proportion present varies with the temperature, the direction of the wind, and other circumstances, but is generally greater in summer than in winter. There are various means by which the moisture in the air may be indicated and its quantity estimated, affording principles for the construction of different hygrometers or hygrometers.

1st. Many solid substances swell on imbibing moisture, and contract again on drying, such as wood, parchment, hair, and most dry organic substances. The hygrometer of Deluc consisted of an extremely thin piece of whalebone, which in expanding and contracting moved an index. The principle of this instrument is illustrated in the transparent shavings of whalebone cut into figures, which bend and crumple up when laid upon the warm hand. Saussure made use of human hair boiled in caustic ley, as a hygrometric body, and it appears to answer better than any other substance of the class. Instruments of this kind are graduated experimentally from observations made on placing them in air kept at a known state of dryness by the presence of deliquescent salts. But all such instruments alter in their indications after a time, and should be viewed as hygrometers rather than hygrometers.



2ndly. The degree of dryness of the air may be judged of by the rapidity of evaporation. Leslie made use of his differential thermometer as a hygrometer, covering one of the bulbs with muslin, and keeping it constantly moist by means of a wet thread from a cup of water placed near it. The evaporation of the moisture cools the ball and occasions the air in it to contract. This instrument gives useful information in regard to the rapidity of evaporation, or the drying power of the air, but does not indicate directly the quantity of moisture in the air. The *wet-bulb* hygrometer

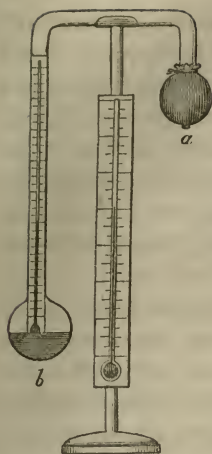
more commonly used, acts on the same principle, but consists of two similar and very delicate mercurial thermometers, the bulb of one of which *a* is kept constantly moist, while the bulb of the other *b* is dry. The wet thermometer always indicates a lower temperature than the dry one, unless when the air is fully saturated with moisture and no evaporation from the moist bulb takes place. In making an observation, the instrument is generally placed, not in absolutely still air, but in an open window where there is a slight draft.

3rdly. The most simple mode of ascertaining the absolute quantity of vapour in the air, is to cool the air gradually, and note the degree of temperature at which it begins to deposit moisture, or ceases to be capable of sustaining the whole quantity of vapour which it possesses. The air is saturated with vapour, for this particular degree of temperature, which is called its *dew-point*. The saturating quantity of vapour for the degree of temperature indicated, may then be learned by reference to a table of the tension of the vapour of water at different temperatures.* It is the absolute quantity of vapour which the air at the time of the observation possesses. The dew-point may be ascertained most accurately by exposing to the air a thin cup of silver or tin-plate containing water so cold as to occasion the condensation of dew upon the metallic surface. The water in the cup is stirred with the bulb of a small thermometer, and as the temperature gradually rises, the degree is noted at which the dew disappears from the surface of the vessel. The temperature at which this occurs may be taken as the dew-point. Water may always be cooled sufficiently in summer, to answer for an experiment of this kind by dissolving pounded sal-ammoniac in it.

The dew point may be observed much more quickly by means of the elegant hygrometer of Professor Daniell.† This instrument (see Figure) consists of two balls, connected by a syphon and containing a quantity of ether, from which the air has been expelled by the same means as in the cryophorus of Dr. Wollaston, (page 63). One of the arms of the syphon tube contains a small thermometer, with its scale, which should be of white enamel; the bulb of the thermometer de-

* Such a table will be given in an Appendix.

† Daniell's Meteorological Essays, p. 147.



scends into the ball *b*, at the extremity of this arm, and is placed, not in the centre of the ball, but as near as possible to some point of its circumference. A zone of this ball is gilt and burnished, so that the deposition of dew may easily be perceived upon it. The other ball *a*, is covered with muslin. When an observation is to be made, this last ball is moistened with ether which is supplied slowly by a drop or two at a time. It is cooled by the evaporation of the ether and becomes capable of condensing the vapour of the included fluid, and thereby occasions evaporation in the opposite ball *b*, containing the thermometer. The temperature of the ball *b*, should be thus reduced in a gradual manner, so that the degree of the thermometer at which dew begins to be deposited on the metallic part of the surface of the ball may be observed with precision. The temperature of *b* being thereafter allowed to rise, the degree at which the dew disappears from its surface may likewise be noted. It should not differ much from the temperature of the deposition, and will probably give the dew point more correctly, although, strictly speaking, the mean between the two observations should be the true dew point. It is convenient to have a second thermometer in the pillar of the instrument, for observing the temperature of the air at the time.

A less expensive instrument is constructed by Mr. Jones of London, which appears to indicate the dew point with tolerable accuracy. It consists of a delicate mercurial thermometer, of which the whole bulb, with the exception of about one-fourth of its surface, is covered with muslin. The bulb is cooled by the application of ether to the coated surface, and the temperature observed at which dew first makes its appearance upon the naked part of the bulb. Mr. Foggo, of Leith, finds the indications of this instrument to be trustworthy,* but a preference is given, by most observers, to the original instrument of Daniell.

The indications of the *wet-bulb* hygrometer first described are discovered by simple inspection. It is, therefore, a problem of

* Brewster's Journal, VII, 36.

the greatest importance to deduce from them the dew point, or the tension of the vapour in the air, by an easy rule. Could this inference be made with certainty, the wet-bulb hygrometer is so commodious that it would supersede all others. I shall place below the formula of Dr. August, which after constant application for the last ten years, has received the general sanction of the philosophers of Berlin. It was employed by Humboldt and G. Rose in their recent expedition to Siberia, and (as I was assured by the latter) with excellent effect.*

In evaporating by means of hot air, as in drying goods in the ordinary bleachers' stove, which is heated by flues from a fire carried along the floor, it should be kept in mind that a certain time must elapse before air is saturated with humidity. Mr. Daniell has observed that a few cubic inches of dry air con-

* Dr. August's formula for deducing the tension of vapour in the air from the temperature indicated by a wet and dry thermometer :

Let x = the tension of vapour in the atmosphere, expressed in Parisian lines, to be found.

e' = tension of vapour at the temperature indicated by the wet thermometer, in Parisian lines, taken from a table.

t = the temperature of the dry thermometer, by Reaumur's scale.

t' = temperature of wet thermometer, by the same scale.

b = the height of the barometer in Parisian lines, the normal height being 336 lines.

Then, for temperatures above zero Reaumur,

$$x = e' - \frac{3}{8} (t - t') - 0.0011 (336 - b) \cdot (t - t')$$

For temperatures below zero Reaumur,

$$x = e' - \frac{1}{8} (t - t') - 0.001 (336 - b) \cdot (t - t')$$

This formula is very simple in its application, as will be seen by a particular example.

Professor Erman made the following observation, May 20, 1827, 2½ A.M.

Dry thermometer, 19°.1 Reaumur.

Wet thermometer, 11°.1 „

Difference of temperature, 8 degrees.

The tension of vapour at 11°.1 is 5.56 Parisian lines ; from which subtract $\frac{3}{8}$ of the difference of temperature, which in this case is the number 3.00. The subtraction gives 2.56 Parisian lines. But the barometer stood 2 lines higher than 336 ; there is therefore $0.0022 \times 8 = 0.02$, to subtract from 2.56 ; which gives 2.54 Parisian lines as the tension of the vapour in the air at the time of observation. The above formulæ are deduced from the expressions

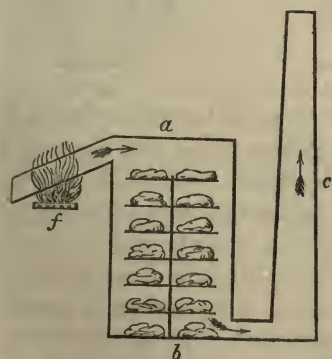
$$x = e' - \frac{0.558(t - t')b}{512 - t'} ; \text{ and}$$

$$x = e' - \frac{0.558(t - t')b}{572 - t'} ;$$

where 512 is the latent heat of vapour at 0° Reaumur.—(*Ueber die Fortschritte der Hygrometrie, von Dr. E. F. August, Berlin 1830.*)

tinue to expand for an hour or two, when exposed to water at the temperature of the air. At high temperatures, the diffusion of vapour into air is more rapid; but still it is not at all instantaneous. Hence, in such a drying stove, means ought to be taken to repress rather than to promote the exit of the hot air; otherwise a loss of heat will be occasioned by the escape of the air, before it is saturated with humidity. The greatest advantage has been derived from closing such a stove as perfectly as possible at the top, and only opening it after the goods are dried and about to be removed, in order to allow of a renewal of the air in the chamber between each operation. In evaporating water by heated air, the vapour itself carries off exactly the same quantity of heat as if it were produced by boiling the water at 212° , while the air associated with it likewise requires to have its temperature raised, and therefore occasions an additional consumption of heat. Hence water can never be evaporated by air in a drying stove with so small an expenditure of fuel as in a close boiler.

When bodies to be dried do not part with their moisture freely, but in a gradual manner, as is the case with roots, and most organic substances, the hot air to dry them may be greatly economized by a particular mode of applying it, which is practised in the madder-stove. The principle of this drying stove

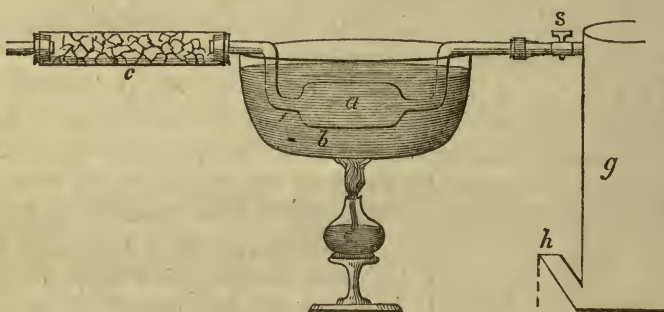


is illustrated by the annexed figure, in which *a b* represents a tight chamber, having two openings, one near the roof, by which hot air is admitted into the chamber, and another at the bottom, by which the air escapes into the tall chimney *c*. The chamber contains a series of stages, from the floor to the roof, on the lowest of which sacks, half filled with the damp madder roots,

are first placed. In proportion as the roots dry, the bags are raised from stage to stage, till they arrive at the highest stage, where they are exposed to the air when hottest and most desiccating. As the dried roots are removed from the top, new roots are introduced below, and passed through in the same manner. Here the dry and hot air, after taking all the moisture

which the roots on the highest stage will part with, descends and is still capable of abstracting a second quantity of moisture from the roots on the next, and so on, as it proceeds, till it passes away into the chimney absolutely saturated with moisture, after having reached the bottom of the chamber.

It is frequently an object to dry a small quantity of a substance most completely (such as an organic substance for analysis) at some steady temperature, such as 212° . This is effected by the following simple and elegant arrangement contrived by M. Liebig. The substance to be dried is introduced, (in the state of a powder if possible) into a short glass cylinder *a*, which may be three inches in length, and one and a half inch in diameter, or any other convenient size, and of which the two ends are terminated by open tubes, bent as represented in the figure. The vessel *a* is immersed in a water-bath *b*, which may



be kept boiling by a lamp below. One of the tubes from *a* is connected by means of a short caoutchouc tube with the upper stopcock *s*, of a gas-holder *g*, or any similar vessel, filled with water. The lower opening *h*, of the gas-holder is left open, so that water can escape by it in proportion as air is admitted by *s*, which air must pass through *a*. The other tube from *a* is connected with a wide glass tube *c*, of eight or ten inches in length, containing fragments of fused chloride of calcium, in passing through which the air is deprived of all moisture before it reaches the substance in *a*. A regulated current of absolutely dry air at 212° may thus be conducted over the substance to be dried.

NATURE OF HEAT.

It is convenient to adopt the material theory of heat in considering its accumulation in bodies, and in expressing quantities of heat and the relative capacities of bodies for heat. Indeed everything relating to the absorption of heat suggests the idea of its substantial existence; for heat, unlike light, is never extinguished when it falls upon a body, but is either reflected and may be farther traced, or is absorbed and accumulated in the body, and may again be derived from it without loss. But the mechanical phenomena of heat, which resemble those of light, may be explained with equal if not greater advantage by assuming an undulatory theory of heat, corresponding with the undulatory theory of light. A peculiar imponderable medium or ether is supposed to pervade all space, through which undulations are propagated, that produce the impression of heat. A hot radiant body is a body possessing the faculty to originate or excite such undulations in the ether or medium of heat, which spread on all sides around it, like the waves from a pebble thrown into still water. Sound is propagated by waves in this manner, but the medium in which they are generally produced, or the usual vehicle of sound, is the air; and all the experiments on the reflection and concentration of heat, by concave reflectors, may be imitated by means of sound. Thus if a watch be placed in the focus of one of a pair of conjugate reflecting mirrors, the waves of air occasioned by its beating emanate from the focus, strike against the mirror, and are reflected from it, so as to break upon the face of the opposite mirror, are concentrated into its focus, and communicate the impression of sound to an ear placed there to receive it. The transmission of heat from the focus of one mirror to the focus of the other may easily be conceived to be the propagation of similar undulations through another and different medium from air, but coexisting in the same space.

In adopting the material theory of heat, we are under the necessity of assuming that there are different kinds of heat, some of which are capable of passing through glass, such as the heat of the sun, while others, such as that radiating from the hand, are entirely intercepted by glass. But on the undulatory theory,

the different properties of heat are referred to differences in the size of the waves, as the differences of colour are accounted for in light. Heat of the higher degrees of intensity, however, admits of a kind of degradation, or conversion into heat of lower intensity, to which we have nothing parallel in the case of light. Thus when the calorific rays of the sun, which are of the highest intensity, pass through glass, and strike a black wall, they are absorbed, and appear immediately afterwards radiating from the heated wall, as heat of low intensity, and are no longer capable of passing through glass. It is as yet an insoluble problem to reverse the order of this change, and convert heat of low into heat of high intensity. We observe the same degradation of heat, or loss of intensity, in condensing steam in distillation. The whole heat of the steam, both latent and sensible, is transferred without loss in that process, to perhaps fifteen times as much condensing water; but the intensity of the heat is reduced from 212° to perhaps 100° Fahr. The heat is not lost; for the fifteen parts of water at 100° are capable of melting as much ice as the original steam. But by no quantity of this heat at 100° can temperature be raised above that degree: we have no means of giving it intensity.

If heat of low is ever changed into heat of high intensity, it is in the compression of gaseous bodies by mechanical means. Let steam of half the tension of the atmosphere, produced at 180° , in a space otherwise vacuous, be reduced into half its volume, by doubling the pressure upon it, and its temperature will rise to 212° . If the pressure be again doubled, the temperature will become 250° , and the whole latent heat of the steam will now possess that high intensity. When air itself is rapidly compressed in a common syringe, we have a remarkable conversion of heat of low into heat of very high intensity.

It may be imagined that the elevation of temperature produced in the friction of hard bodies has a similar origin; that it results from the conversion of heat of low intensity, which the bodies rubbed together possess, into heat of high intensity. But it would be necessary further to suppose that a supply of heat of low intensity to the bodies rubbed can be endlessly kept up, by conduction or radiation, from contiguous bodies, as there appears to be no limit to the production of heat by means of friction.

Count Rumford, by boring a cylinder of cast iron, raised the

temperature of several pounds of cold water to the boiling point. Sir H. Davy succeeded in melting two pieces of ice in the vacuum of an air pump, by making them rub against each other, while the temperature of the air pump itself and the surrounding atmosphere was below 32° . M. Haldot observed that when the surface of the rubber was rough, only half as much heat appeared as when the rubber was smooth. When the pressure of the rubber was quadrupled, the proportion of heat evolved was increased seven fold. When the rubbing apparatus was surrounded by bad conductors of heat, or by non-conductors of electricity, the quantity of heat evolved was diminished.* No heat whatever is produced by the friction of fluids upon each other, or upon solids; nor by the friction of gases upon liquids or solids.

One other point only connected with the nature of heat remains, to which there is at present occasion to allude—the existence of a repulsive property in heat. Such a repulsive power in heated bodies is inferred to exist from the appearance of extreme mobility which many fine powders assume, such as precipitated silica, on being heated nearly to redness. Mr. Forbes also attributes to such a repulsion the vibrations which take place between metals unequally heated, and the production of tones, to which allusion has already been made. But this repulsive power was rendered conspicuous, and even measurable, by Mr. Powell, in the case of glass lenses, of very slight convexity, pressed together. On the application of heat, a separation of the glasses, through extremely small but finite spaces, was indicated by a change in the tints which appear between the lenses, and which depend upon the thickness of the included plate of air. This repulsion between heated surfaces appears to be promoted by whatever tends to the more rapid communication of heat.†

* Nicholson's Journal, XXVI, 30.

† Phil. Trans. 1834, p. 485.

CHAPTER II.

LIGHT.

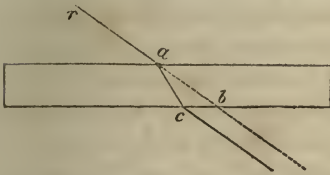
THE mechanical properties of light constitute the science of optics, and belong, therefore, to physics, and not to chemistry. But it may be useful, by a short recapitulation, to recal them to the memory of the reader.

1. The rays of light emanate with so great velocity from the sun, that they occupy only $7\frac{1}{2}$ minutes in traversing the immense space which separates the earth from that luminary. They travel at the rate of 192,500 miles in a second, and would, therefore, move through a space equal to the circumference of our globe in 1-8th of a second. They are propagated continually in straight lines, and spread or diverge at the same time; so that their density diminishes in the direct proportion of the square of their distance from the sun. Hence, if the earth were at double its present distance from the sun, it would receive only one-fourth of the light; at three times its present distance, one-ninth; at four times its present distance, one-sixteenth, &c.

2. When the solar rays impinge upon a body, they are reflected from its surface, and bound off as an elastic ball, striking against the same surface in the same direction, would do; or they are absorbed by the body upon which they fall, and disappear, being extinguished; or lastly, they pass through the body, which in that case is transparent or diaphanous. In the first case, the body becomes visible, appearing white, or of some particular colour, and we see it in the direction in which the rays reach the eye. In the second case, the body is invisible, no light proceeding from it to the eye; or it appears black, if the surrounding objects are illuminated. In the third case, if the body be absolutely transparent, it is invisible, and we see through it the object from which the light was last reflected. But light is often greatly affected in passing through transparent bodies.

3. If light enters such media, of uniform density, perpendicularly to their surface, its direction is not altered; but in pass-

ing obliquely out of one medium into another, it undergoes a change of direction. If the second medium be denser than the first, the ray of light is bent, or *refracted*, nearer to the perpendicular; but in passing out from a denser into a rarer medium, it is refracted from the perpendicular. Thus, when the ray of



light *r*, passing through the air, falls obliquely upon a plate of glass at the point *a*, instead of continuing to move in the same straight line *a b*, it is bent towards the perpendicular at *a*,

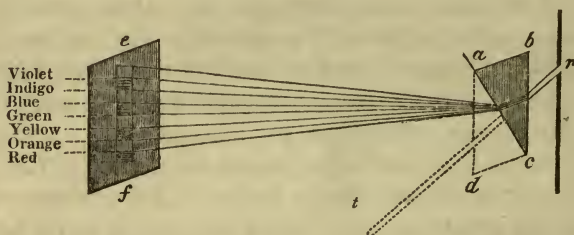
and proceeds in the direction *a c*. The ray is bent to the side on which there is the greatest mass of glass. On passing out from the glass into the air, a rarer medium, at the point *c*, the ray has its direction again changed, and in this case *from* the perpendicular, but still towards the mass of glass. The amount of refraction, generally speaking, is proportional to the density of a body, but combustible bodies possess a higher refracting power than corresponds to their density. Hence the diamond, melted phosphorus, naphtha, and hydrogen gas, exhibit this effect upon light in a greater degree than other transparent bodies. Dr. Wollaston had recourse to this refracting power as a test of the purity of some substances. Thus, genuine oil of cloves had a refracting power expressed by the number 1535, while that of an impure specimen was not more than 1498.

4. In passing through many crystallized bodies, such as Iceland spar, a certain portion of light is refracted in the usual way, and another portion undergoes an extraordinary refraction, in a plane parallel to the diagonal which joins the two obtuse angles of the crystal. Such bodies are said to *refract doubly*, and exhibit a double image of any body viewed through them.

5. Reflected and likewise doubly refracted light assume new properties. Common light, reflected from the surface of glass, or any bright surface non-metallic, is, more or less of it, converted into what is called *polarized* light. If it be reflected at one particular angle of incidence, $56^{\circ} 45'$, it is *all* changed into polarized light; and the farther the angle of reflection deviates from 56° , on either side, the less is polarized, and the more remains common light. 56° is the maximum polarizing angle for glass; $52^{\circ}.45'$ for water. The light is said to be *polarized*, from certain properties which it assumes, which seem to indicate

that the ray, like a magnetic bar, has sides in which reside peculiar powers. One of these new properties is, that when it falls upon a second glass plate, it is not reflected in the same way as common light. If the plane of the second reflector is *perpendicular* to the first, and the ray fall at an angle of 56° , it is not reflected at all, it *vanishes*; but if *parallel*, it is entirely reflected. Polarized light appears to possess some most extraordinary properties, in regard to vision, of useful application. It is said that a body which is quite transparent to the eye, and which appears upon examination to be as homogeneous in its structure as it is in its aspect, will yet exhibit, under polarized light, the most exquisite organization. As an example of the utility of this agent in exploring mineral, vegetable and animal structures, Sir D. Brewster refers to the extraordinary structure of the minerals apophyllite and analcime; to the symmetrical and figurate disposition of siliceous crystals in the epidermis of equisetaceous plants, and to the wonderful variations of density in the crystalline lenses, and the integuments of the eyes of animals, which polarized light renders visible.*

6. *Decomposition of light.* When a beam of light from the



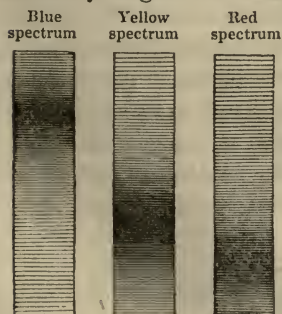
sun is admitted into a dark room, by a small aperture r in a window shutter, and is intercepted in its passage by a wedge or solid angle of glass abc , it is refracted as it enters, and a second time as it issues from the glass; and instead of forming a round spot of white light, as it would have done if allowed to proceed in its original direction rt , it illuminates with several

* Reports of the British Association, vol. i. Report upon Optics, by Sir D. Brewster,

colours an oblong space of a white card *ef*, properly placed to receive it. The solid wedge of glass is called a prism, and the oblong coloured image on the card, the solar spectrum. Newton counted seven bands of different colours in the spectrum, which, as they succeed each other from the upper part of the spectrum represented in the figure, are violet, indigo, blue, green, yellow, orange and red. The beam of light admitted by the aperture in the window-shutter has been separated in passing through the prism into rays of different colours, and this separation obviously depends upon the rays being unequally refrangible. The blue rays are more considerably refracted or deflected out of their course, in passing through the glass, than the yellow rays, and the yellow rays than the red. Hence the violet end is spoken of as the most refrangible, and the red as the least refrangible end of the spectrum.

The coloured bands of the spectrum differ in width, and are shaded into each other; and it is not to be supposed that there are really rays of seven different colours. Sir D. Brewster has established, in a recent analysis of solar light, that there are rays of three colours only, blue, yellow and red, which were well known to artists to be the three primary colours, of which all others are compounded.

A certain quantity of white light, and a portion of each of the primary rays, may be found at every point from the top to the bottom of the spectrum. But each of the primary rays predominates at a particular part of the spectrum. This point is, for the blue rays, near the top of the spectrum; for the yellow rays, somewhat below the middle; and for the red rays, near the bottom of the spectrum. Hence, there exist rays of each colour of every degree of refrangibility; but the great proportion of



annexed figures.

the yellow rays is more refrangible than the red, and the great proportion of the blue more refrangible than either the yellow or red. The compound spectrum which we observe, is in fact produced by the superposition of three simple spectra, a blue, a yellow, and a red spectrum. The distribution of the rays in each of these simple spectra is represented by the shading in the

Of the seven different coloured bands into

which Newton divided the spectrum, not one is a pure colour. The orange is produced by a predominance of the yellow and red rays ; the green, by the yellow and blue rays, and the indigo and violet are essentially blue, with different proportions of red and yellow.*

By placing a second prism *adc*, in a reversed position, in contact with the first prism, the colours disappear, and we have a spot of white light, as if both prisms were absent. The three coloured rays of the spectrum, therefore, produce white light by their union.

On examining the solar spectrum, Dr. Thomas Young observed that it is crossed by several dark lines, that is, that there are interruptions in the spectrum, where there is no light of any colour. Fraunhofer subsequently found that the lines in the spectrum of solar light were much more numerous than Dr. Young had imagined, while the spectrum of *artificial* white flames contains all the rays which are thus wanting. One of the most notable is a double dark line in the yellow, which occurs in the light of the sun, moon, and planets. In the light of the fixed stars, Syrius and Castor, the same double line does not occur ; but one conspicuous dark line in the yellow, and two in the blue. The spectrum of Pollux, on the contrary, is the same as that of the sun. Now a very recent discovery of Sir D. Brewster has given these observations an entirely chemical character. He has found that the white light of ordinary flames requires merely to be sent through a certain gaseous medium (nitrous acid vapour) to acquire more than a thousand dark lines in its spectrum. He is hence led to infer that it is the presence of certain gases in the atmosphere of the sun, which occasions the observed deficiencies in the solar spectrum. We may thus have it yet in our power to study the nature of the combustion which lights up the suns of other systems. (Report upon Optics.)

The rays of *heat* are distributed very unequally throughout the luminous spectrum ; most heat being found associated with the red or least refrangible luminous rays, and least with the violet rays. Indeed when the solar beam is decomposed by a prism of a highly diathermanous material, such as rock salt,

* Sir David Brewster, On a new analysis of the solar light, indicating three primary colours, forming coincident spectra of equal length.—Edinburgh Phil. Trans. vol. xii. p. 123,

the rays of heat are found to extend, and to have their point of maximum intensity considerably beyond the visible spectrum, on the side of the red ray. Hence, although there are calorific rays of all degrees of refrangibility, the great proportion of them are even less refrangible than the least refrangible luminous rays. It is observed that the least refrangible rays are absorbed in greatest proportion in passing through bodies which are not highly diathermanous, such as crown-glass and water. Hence prisms of these substances, allowing only the more refrangible rays of heat to pass, give a spectrum which is hottest in the red, or perhaps even in the yellow ray, and possesses little or no heat beyond the border of the red ray. The inequality in refrangibility existing between the rays of heat and of light is decisive of the fact, that they are peculiar rays, that can be separated, although associated together in the sun-beam. Indeed, Melloni finds that light from both solar and terrestrial sources is divested of all heat by passing successively through water, and a glass, coloured green by the oxide of copper, being incapable as it issues from these media of affecting the most delicate thermoscope.

The light of the sun is capable of inducing certain chemical changes which do not depend either upon its luminous or calorific rays, but upon the presence of what are called *chemical rays*. Thus chlorine gas, under the influence of light, is capable of decomposing water, combining with its hydrogen, and liberating oxygen; and the chlorine in the freshly precipitated chloride of silver has a similar effect; but the oxygen in the last case, instead of being set free, combines with the silver, and causes the colour of the compound to change from white to black. The moist chloride of silver is darkened more rapidly by the violet than by the red rays of the spectrum; but this change is produced upon it even when carried a little way out of the visible spectrum on the side of the violet ray. The rays found in that situation are, therefore, more refrangible than any other kind of rays in the spectrum. Their characteristic effect is to promote those chemical decompositions in which oxygen is withdrawn from water and other oxides, and hence they are sometimes named *de-oxidizing rays*. These rays were likewise supposed to communicate magnetism to steel needles exposed to them but this opinion is no longer tenable.

CHAPTER III.

CHEMICAL NOMENCLATURE AND NOTATION.

THERE are at present fifty-four substances known, which are simple, or contain one kind of matter only. Their names are given in the following tables, together with certain useful numbers which express the quantities by weight, according to which the different elements combine with each other. The letter or symbol annexed to the name is employed to represent these particular quantities of the elements, or their combining proportions.

TABLE I.
NAMES OF ELEMENTS

WITH THEIR SYMBOLS AND LEAST COMBINING PROPORTIONS.

Names of Elements.	Symbols	Equivalents.		Names of Elements.	Symbols	Equivalents.	
		O as 100.	H as 1.			O as 100.	H as 1.
Oxygen.....	O	100.00	8.01	Cobalt	Co	368.99	29.57
Hydrogen.....	H	12.4795	1.00	Nickel.....	Ni	369.68	29.62
Nitrogen.....	N	177.04	14.19	Copper (Cuprum) ..	Cu	395.70	31.71
Carbon.....	C	76.44	6.13	Bismuth.....	Bi	886.92	71.07
Sulphur.....	S	201.17	16.12	Lead (Plumbum) ..	Pb	1294.50	103.73
Selenium.....	Se	494.58	39.63	Tin (Stannum) ..	Sn	735.29	58.92
Phosphorus... ..	P	392.28	31.44	Cerium.....	Ce	574.70	46.05
Boron.....	B	136.25	10.91	Uranium.....	U	2711.36	217.26
Silicon.....	Si	277.31	22.22	Arsenic.....	As	940.08	75.34
Chlorine.....	Cl	442.65	35.47	Antimony (Sti-			
Iodine.....	I	1579.50	126.57	biüm).....	Sb	1612.90	129.24
Bromine.....	Br	978.31	78.39	Chromium.....	Cr	351.82	28.19
Fluorine.....	F	233.80	18.74	Vanadium.....	V	856.89	68.66
Potassium (Kali-				Molybdenum... ..	Mo	598.52	47.96
um).....	K	489.92	39.26	Tungsten (Wol-			
Sodium (Natroni-				fram).....	W	1183.00	94.80
um).....	Na	290.90	23.31	Columbium			
Lithium.....	L	80.33	6.44	(Tantalum) ..	Ta	2307.43	184.90
Barium.....	Ba	856.88	68.66	Tellurium.....	Te	801.76	64.25
Strontium.....	Sr	547.29	43.85	Titanium.....	Ti	303.66	24.33
Calcium.....	Ca	256.02	20.52	Osmium.....	Os	1244.49	99.72
Magnesium.....	Mg	158.35	12.69	Mercury (Hy-			
Aluminum.....	Al	171.17	13.72	drargyrum....	Hg	1265.82	101.43
Glucinum.....	G	331.26	26.54	Silver (Argen-			
Zirconium.....	Zr	420.20	33.67	tum).....	Ag	1351.61	108.30
Thorium.....	Th	744.90	59.83	Gold (Aurum)..	Au	2486.03	199.21
Yttrium.....	Y	402.51	32.25	Platinum.....	Pl	1233.50	98.84
Manganese.....	Ma	345.89	27.72	Palladium.....	Pd	665.90	53.36
Iron (Ferrum) ..	Fe	339.21	27.18	Rhodium.....	R	651.39	52.20
Zinc.....	Zn	403.23	32.31	Iridium... ..	Ir	1233.50	98.84
Cadmium.....	Cd	696.77	55.83				

TABLE II.

NAMES OF ELEMENTS

ARRANGED ALPHABETICALLY WITH THEIR SYMBOLS AND LEAST
COMBINING PROPORTIONS. .

Names of Elements.	Symbols	Equivalents.		Names of Elements.	Symbols	Equivalents.	
		O as 100.	H as 1.			O as 100.	H as 1.
Aluminum	Al	171.17	13.72	Molybdenum . . .	Mo	598.52	47.96
Antimony (Stibium)	Sb	1612.90	129.24	Nickel	Ni	369.68	29.62
Arsenic	As	940.08	75.34	Nitrogen	N	177.04	14.19
Barium	Ba	856.88	68.66	Osmium	Os	1244.49	99.72
Bismuth	Bi	886.92	71.07	Oxygen	O	100.00	8.01
Boron	B	136.25	10.91	Palladium	Pd	665.90	53.36
Bromine	Br	978.31	78.39	Phosphorus	P	392.28	31.44
Cadmium	Cd	696.77	55.83	Platinum	Pl	1233.50	98.84
Calcium	Ca	256.02	20.52	Potassium (Kalium)	K	489.92	39.26
Carbon	C	76.44	6.13	Rhodium	R	651.39	52.20
Cerium	Ce	574.70	46.05	Selenium	Se	494.58	39.63
Chlorine	Cl	442.65	35.47	Silicon	Si	277.31	22.22
Chromium	Cr	351.82	28.19	Silver (Argentum)	Ag	1351.61	108.30
Cobalt	Co	368.99	29.57	Sodium (Natrium)	Na	290.90	23.31
Columbium (Tantalum)	Ta	2307.43	184.90	Strontium	Sr	547.29	43.85
Copper (Cuprum)	Cu	395.70	31.71	Sulphur	S	201.17	16.12
Fluorine	F	233.80	18.74	Tellurium	Te	801.76	64.25
Glucinum	G	331.26	26.54	Thorium	Th	744.90	59.83
Gold (Aurum)	Au	2486.03	199.21	Tin (Stannum)	Sn	735.29	58.92
Hydrogen	H	12.4795	1.00	Titanium	Ti	303.66	24.33
Iodine	I	1579.50	126.57	Tungsten (Wolfram)	W	1183.00	94.80
Iridium	Ir	1233.50	98.84	Vanadium	V	856.89	68.66
Iron (Ferrum)	Fe	339.21	27.18	Uranium	U	2711.36	217.26
Lead (Plumbum)	Pb	1294.50	103.73	Yttrium	Y	402.51	32.25
Lithium	L	80.33	6.44	Zinc	Zn	403.23	32.31
Magnesium	Mg	158.35	12.69	Zirconium	Zr	420.20	33.67
Manganese	Mn	345.89	27.72				
Mercury (Hydargyrum)	Hg	1265.82	101.43				

TABLE III.

ALPHABETICAL ARRANGEMENT OF SYMBOLS.

O as 100.			H as 1.			O as 100.			H as 1.		
Ag indicates	1351.61		108.30 Silver (Argentum)			N indicates	177.04		14.19 Nitrogen		
Al	171.17		13.72 Aluminum			Na	290.90		23.31 Sodium (Natronium)		
As	940.08		75.34 Arsenic			Ni	369.68		29.62 Nickel		
Au	2486.03		199.21 Gold (Aurum)			O	100.00		8.01 Oxygen		
B	136.25		10.91 Boron			Os	1244.49		99.72 Osmium		
Ba	856.88		68.66 Barium			P	392.28		31.44 Phosphorus		
Bi	886.92		71.07 Bismuth						103.73 Lead (Plumbum)		
Br	978.31		78.39 Bromine			Pb	1294.50		53.36 Palladium		
C	76.44		6.13 Carbon			Pd	665.90		98.84 Platinum		
Ca	256.02		20.52 Calcium			Pl	1233.50		52.20 Rhodium		
Cd	696.77		55.83 Cadmium			R	651.39		16.12 Sulphur		
Ce	574.70		46.05 Cerium			S	201.17		129.24 Antimony (Stibium)		
Cl	442.65		35.47 Chlorine			Sb	1612.90		39.63 Selenium		
Co	358.99		29.57 Cobalt			Se	494.58		22.22 Silicon		
Cr	351.82		28.19 Chromium			Si	277.31		58.92 Tin, (Stannum)		
Cu	395.70		31.71 Copper (Cuprum)			Sn	735.29		43.85 Strontium		
F	233.80		18.74 Fluorine			Sr	547.29		184.90 Columbium (Tantalum)		
Fe	339.21		27.18 Iron (Ferrum)			Ta	2307.43		64.25 Tellurium		
G	331.26		26.54 Glucinum			Te	801.76		59.83 Thorium		
H	12.4795		1.00 Hydrogen			Th	744.90		24.33 Titanium		
Hg	1265.82		101.43 Mercury (Hydragrum)			Ti	303.66		217.26 Uranium		
I	1579.50		126.57 Iodine			U	2711.36		68.66 Vanadium		
Ir	1233.50		98.84 Iridium			V	856.89		94.80 Tungsten (Wolfram)		
K	489.92		39.26 Potassium (Kalium)			W	1183.00		32.25 Yttrium		
L	80.33		6.44 Lithium			Y	402.51		32.31 Zinc		
Mg	158.35		12.69 Magnesium			Zn	403.23		33.67 Zirconium		
Mn	345.89		27.72 Manganese			Zr	420.20				
Mo	598.52		47.96 Molybdenum								

In the class of simple substances are placed all those bodies which are not known to be compound, on the principle that whatever cannot be decomposed or resolved by any process of chemistry into other kinds of matter, is to be considered as simple. They are the only bodies the names of which are at present independent of any rule. An attempt was, indeed, made on the first introduction of a systematic nomenclature, to make the names of several of them significant; but some confusion in regard to their derivatives was found to be the consequence of this, and many of them being familiar substances, were almost of necessity allowed to retain the names they bear in common language; such as, sulphur, tin, silver, and the other metals known in the arts. To newly discovered elements, however, such names were applied as were suggested by any striking physical property they possessed, or remarkable circumstance in their history. The names of the newer metals, platinum, potassium, vanadium, etc., have a common termination, which serves to distinguish them as metals. Other classes of elementary bodies, resembling each other in certain particulars, are marked in a similar manner; such as the class comprising carbon, boron and silicon, and that composed of chlorine, iodine, bromine, and fluorine.

The names of *compound bodies* are contrived to express their composition, and the class to which they belong, and are founded on a distribution of compounds into three orders, namely: first, compounds of one element with another element, as for instance, oxygen with sulphur in sulphuric acid, or oxygen with sodium in soda, which are called binary compounds. Secondly, combinations of binary compounds with each other, as of sulphuric acid with soda in Glauber's salt, and the salts generally, which are termed ternary compounds. And thirdly, combinations of salts with one another, or double salts such as alum, which are quaternary compounds.

1.—Of the compounds of the first order, the greater number known to the original framers of the chemical nomenclature, contained oxygen as one of their two constituents; and hence, an exclusive importance was attached to that element. Its compounds with the other elementary bodies, may be divided from their properties into: (*a*) the class of neutral bodies and bases; and (*b*) the class of acids.

(*a*) To members of the first class, the generic term *oxide* was

applied, the first syllable of oxygen, with a termination indicative of combination; to which the name of the other element was joined to express the specific compound. Thus a compound of oxygen and hydrogen is *oxide of hydrogen*; of oxygen and potassium, *oxide of potassium*; of which compounds the first or water, is an instance of a neutral oxide; and the second or potash, of a base or alkaline oxide. But the same elementary body often combines with oxygen in more than one proportion, forming two or more oxides; to distinguish which the Greek prefix *proto* (πρῶτος first) is applied to the oxide containing the least proportion of oxygen; *deuto* (δευτερος, second) to the oxide containing more oxygen than the protoxide; and *trito* (τρίτος, third) to the oxide containing still more oxygen than the deutoxide; which last oxide if it contains the largest proportion of oxygen, with which the element can unite to form an oxide, is more commonly named the *peroxide*, from *per* the Latin particle of intensity. Thus the three compounds of the metal manganese and oxygen are distinguished as follows:

Names	Composition	
	Manganese	Oxygen
Protoxide of manganese.	100	29.81
Deutoxide of manganese.	100	43.36
Peroxide of manganese.	100	57.82

As the prefix *per* implies simply the highest degree of oxidation, it may be applied to the second oxide where there are only two, as in the oxides of iron, the second oxide of which is called, indifferently, the deutoxide or peroxide of iron. M. Thénard, in the last edition of his *Traité de Chimie*, avoids the use of the term deutoxide, and confines the application of peroxide to such of these oxides as, like the peroxide of manganese, do not combine with acids. He applies the names *sesquioxide* and *binoxide* to oxides, which are capable of combining with acids, and contain respectively, once and a half and twice as much oxygen as the protoxides of the same metal. He has thus the protoxide, sesquioxide and peroxide of manganese, the protoxide and sesquioxide of iron, the protoxide and binoxide of tin, etc. The sesquioxides of iron and manganese of Thénard, are also named *tritoxides* by some French chemists, as to double the proportion of metal in the protoxides, they possess three times as much oxygen. Certain inferior oxides, which do not combine with acids are called *suboxides*; such as the suboxide of

lead, which contains less oxygen than the oxide distinguished as the protoxide of the same metal.

The compounds of chlorine and certain other elements are distinguished in the same manner as the oxides. Such elements resemble oxygen in several respects, particularly in the manner in which their compounds are decomposed by electricity. Chlorine, for example, like oxygen, proceeds to the positive pole, and is therefore classed with oxygen as an electro-negative substance, in a division of elements grounded on their electrical relations. Thus with the other elementary bodies,

Oxygen	forms	oxides,
Chlorine	„	chlorides,
Bromine	„	bromides,
Iodine	„	iodides,
Fluorine	„	fluorides,
Cyanogen	„	cyanides,
Sulphur	„	sulphurets.

As cyanogen although a compound body comports itself in its combinations like an electro-negative element, its compounds are named in the same manner as the oxides. When several chlorides of the same metal exist, they are distinguished by the same numerical prefixes as the oxides. Thus we have the protochloride and the deutochloride or perchloride of iron; the protochloride, and the bichloride of tin; the application of the prefix *bi* being more generally sanctioned in the case of chlorides than oxides. The compounds of sulphur greatly resemble the oxides, but they are named sulphurets and not sulphides. Berzelius indeed applies the term sulphuret to such binary compounds of sulphur only as are basic or correspond with basic oxides; while sulphide is applied to such as are acid, or correspond with acid oxides. Hence, he has the *sulphuret of potassium*, and the *sulphide of arsenic* and *sulphide of carbon*. Compounds of chlorine are distinguished by him into chlorurets and chlorides, on the same principle; thus he speaks of the *chloruret of potassium* and of the *chloride of phosphorus*. But these distinctions have not been regarded by French or English chemists.

Compounds of carbon and phosphorus with electro-positive elements are named *carburets* and *phosphurets*, as the carburet of iron, the phosphuret of lead. In all such cases it is the name of the electro-negative element, or that which most resembles oxygen, which is placed first in the name of the

compound, and has a termination expressive of combination attached to it. Thus a compound of chlorine and phosphorus is called *chloride of phosphorus*, and not phosphuret of chlorine; of sulphur and carbon, *sulphuret of carbon*, and not carburet of sulphur. The combinations of metallic elements among themselves are distinguished by the general term *alloys*, and those of mercury as *amalgams*.

(b) The binary compounds of oxygen which possess acid properties, are named on a different principle. Thus the acid compound of titanium and oxygen is called *titanic acid*; of chromium and oxygen, *chromic acid*; or the name of the acid is derived from that of the substance in combination with oxygen, with the termination *ic*. Where the same element was known to form two acid compounds with oxygen, the termination *ous* was applied to that which contained the least proportion of oxygen, as in *sulphurous* and *sulphuric acids*. On the discovery of an acid compound of sulphur which contained less oxygen than that already named *sulphurous acid*, it was called *hyposulphurous acid*, (from the Greek *ὑπο*, under) and another new compound, intermediate between the *sulphurous* and *sulphuric acids*, was named *hyposulphuric acid*. On the same principle, an acid containing a greater proportion of oxygen than that already named *chloric acid* was named *hyperchloric acid*, (from the Greek *ὑπερ*, over). The names of the different acid compounds of oxygen and sulphur, which have been referred to for illustration, with the relative proportions of oxygen which they contain, are as follows :

Names.	Composition.	
	Sulphur.	Oxygen.
Hyposulphurous acid	100	49.75
Sulphurous acid	100	99.50
Hyposulphuric acid	100	124.37
Sulphuric acid	100	149.25

This system has been adopted for all analogous acids. An acid of chlorine, containing more oxygen than *chloric acid*, is named *hyperchloric acid*, and other similar compounds, which all contain an unusually large proportion of oxygen are distinguished in the same manner, as *hyperiodic acid* and *permanganic acid*. The *hyperchloric acid* is also sometimes called *perchloric* and *oxichloric*; but these last terms do not seem so suitable as the first.

Another class of acids exists in which sulphur is united with the other element in the place of oxygen. The acids thus formed are called *sulphur-acids*. The names of the corresponding oxygen acids are sometimes applied to these, with the prefix *sulpho*, as *sulpho-arsenious* and *sulpho-arsenic* acids, which resemble arsenious and arsenic acids respectively in composition, but contain sulphur instead of oxygen. Lastly, certain substances, such as chlorine, sulphur and cyanogen, form acids with hydrogen, which are called hydrogen acids, or *hydracids*. In these acid compounds the names of both constituents appear as in the terms *hydrochloric acid*, *hydrosulphuric acid*, and *hydrocyanic acid*. Thénard has lately altered these names to *chlorhydric*, *sulphohydric* and *cyanhydric acids*, which are certainly preferable terms.

2.—Compounds of the second order, or salts, are named according to the acid they contain, the termination *ic* of the acid being changed into *ate*, and *ous* into *ite*. Thus a salt of sulphuric acid is a *sulphate*; of sulphurous acid, a *sulphite*; of hyposulphurous acid, a *hyposulphite*; of hyposulphuric acid, a *hyposulphate*; and of hyperchloric acid, a *hyperchlorate*; and the name of the oxide indicates the species, as the sulphate of the oxide of silver, or the sulphate of silver, for the oxide of the metal being always understood it is unnecessary to express it, unless when more than one oxide of the same metal combines with acids, as sulphate of the protoxide of iron, and sulphate of the peroxide of iron. These salts are sometimes called proto-sulphate and persulphate of iron, where the prefixes proto and per refer to the degree of oxidation of the iron. The two oxides of iron are named *ferrous oxide* and *ferric oxide* by Berzelius, and the salts referred to, the ferrous sulphate, and the ferric sulphate. The names stannous sulphate and stannic sulphate express in the same way, the sulphate of the protoxide of tin, and the sulphate of the peroxide of tin. But such names, although truly systematic and replacing very cumbrous expressions, involve too great a change in chemical nomenclature to be speedily adopted. Having found its way into common language, chemical nomenclature can no longer be altered materially without great inconvenience. It must be learned as a language, and not be viewed and treated as the expression of a system. A *super-sulphate* contains a greater proportion of acid than the sulphate or neutral sulphate; a *bi-sulphate* twice as

much, and a *sesqui*-sulphate once and a half as much as the neutral sulphate; while a *sub*-sulphate contains a less proportion than the neutral salt; the prefixes referring in all cases to the proportion of acid in the salt, or to the *electro-negative* ingredient, as in the case of oxides. The excess of base in sub-salts is sometimes indicated by Greek prefixes expressive of quantity, as *di*-chromate of lead, *tris*-acetate of lead, but this deviation from rule is apt to lead to confusion. If a precise expression for such subsalts were required, it would be better to say the bibasic subchromate of lead, the tribasic subacetate of lead. But the names of both acid and basic salts are less in accordance with correct views of their constitution, than the names of any other class of compounds.

Combinations of water with other oxides are called *hydrates*, as hydrate of potash, hydrate of boracic acid.

3.—In the names of quarternary compounds or of double salts, the names of the constituent salts are expressed, thus: *sulphate of alumina and potash* is the compound of the sulphate of alumina with the sulphate of potash; *tartrate of potash and soda*, the compound of the tartrate of potash with the tartrate of soda; the name of the acid being expressed only once, as it is the same in both of the constituent salts. The names alum and Rochelle salt which have been assigned by common usage to the same double salts, are likewise received in scientific language. The *chloride of platinum and potassium* expresses, in the same way a compound of chloride of platinum with chloride of potassium. An oxichloride, such as the *oxichloride of mercury*, is a compound of the oxide with the chloride of the same metal.

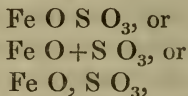
The present nomenclature does not furnish precise expressions for many new classes of compounds, the existence of which was not contemplated by its inventors, and many of its names express theoretical views of the constitution of bodies which are doubtful, and not admitted by all chemists. But its deficiencies are supplied, and the composition of bodies more accurately represented, in certain written expressions, or chemical formulæ, which are also employed to denote particular substances, and which form a valuable supplement to the nomenclature still generally used. These formulæ are constructed on the simplest principles, and besides supplying the deficiencies of the old nomenclature, they at once exhibit to the eye the composition of bodies, and afford a mechanical aid in observing

relations in composition, of the same kind as the use of figures in the comparison of arithmetical sums.

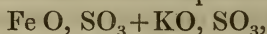
Symbols of the elements. Each elementary substance is represented by the initial letter of its Latin name as will be seen by reference to Table I, page 94; but when the names of two or more elements begin with the same letter, a second in a smaller character is added for distinction; thus oxygen is represented by the letter O, the metal osmium by Os, fluorine by F, and iron (ferrum) by Fe; small letters, it is to be observed, never being significant of themselves, but employed only in connexion with the large letters as distinctive adjuncts. These symbols represent, at the same time, certain relative quantities of the elements, the letter O expressing not oxygen indefinitely, but 100 parts by weight of oxygen, and Fe, 339 parts by weight of iron, or any other quantities of these two substances which are in the proportion of these numbers; 8 parts of oxygen, for instance, and 27.18 of iron. It will immediately be explained that the elementary bodies combine with each other in certain proportional quantities only, which may be expressed by one or other of the two series of numbers placed against the names of the elements in the tables (pages 94, 95, 96). These quantities are conveniently spoken of, as the equivalent quantities, or *equivalents*, *combining proportions* or *proportions* of the elements. The symbol or letter, of itself representing *one* equivalent of the element, several equivalents are represented by repeating the symbol, or by placing figures before it, thus Fe Fe, or 2 Fe, and 3 O, which mean two equivalents of iron and three of oxygen; or small figures are placed either above or below the symbol, and to the right, thus Fe^2 , O^3 , or Fe_2 , O_3 , which expressions are of the same value as the former, but are used only when symbols are placed together in the formulæ of compounds. Two equivalents of an element are often expressed by placing a dash through, or under its symbol, as 2C, by $\text{C}-$ or C_- , but such abbreviations will not be made use of in the present work. The substance represented by any symbol, which occurs to the reader in the following pages, may be learned by reference to the alphabetical arrangement of symbols, page 96.

Formulæ of compounds. The collocation of symbols expresses combination; thus Fe O represents a compound of one equivalent or proportion of iron, and one of oxygen, or the protoxide of iron; SO_3 , a compound of one equiva-

lent of sulphur, and three of oxygen, that is one equivalent of sulphuric acid; and sulphate of iron itself consisting of one equivalent of each of the preceding compounds, may be represented as follows:

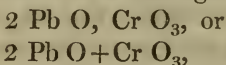


The sign plus (+) or the comma, being introduced in the second and third formulæ, to indicate a distribution of the elements of the salt into its two proximate constituents, oxide of iron, and sulphuric acid, which is not so distinctly indicated in the first formula. It may often be advantageous to make use of both the comma and the plus sign in the same formula, and then it would be a beneficial practice to use them as in the following formula for the double sulphate of iron and potash:

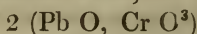


in which the comma is employed to indicate combination more intimate in degree, or of a higher order than the plus sign, namely, of the oxide with the acid in each salt, while the combination of the two salts themselves is expressed by the sign +.

The small figures in the preceding formulæ affect only the symbol or letter to which they are immediately attached. Larger figures placed before and in the same line with the symbols apply to the *compound* expressed by the symbols. Thus 3 S O_3 , means three equivalents of sulphuric acid; 2 Pb O , two equivalents of oxide of lead. But the interposition of a comma or plus sign prevents the influence of the figure extending farther, thus

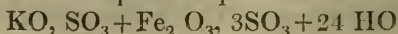


is two proportions of oxide of lead, and one of chromic acid, or the sub-chromate of lead. To make the figure apply to symbols separated by the comma or plus sign, it is necessary to enclose all that is to be affected within brackets, and place the figure before them. Thus,

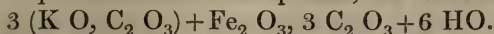


means two proportions of the chromate of lead. The following formulæ of two double salts with their water of crystallization, exhibit the application of these rules:

Iron-alum, or the sulphate of peroxide of iron and potash,

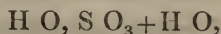


Oxalate of peroxide of iron and potash,



It will be found to conduce to perspicuity, to avoid either connecting two formulæ of different substances not in combination, by the sign plus, or allowing them to be separated merely by a comma, as the plus and comma *between* symbols or formulæ are conventionally understood to unite the formulæ into one, and to express combination; and indeed it is advisable to write every complete formula apart, and in a line by itself, if possible.

The only other circumstance to be attended to in the construction of such formulæ is the *arrangement* of the symbols or letters, which is not arbitrary. In naming a binary compound, such as oxide of iron, chloride of potassium, etc. we announce first the oxygen or element most resembling it in the compound, and which is called the *electro-negative* ingredient; but in the formulæ of the same bodies, it is the other or the *electro-positive* element which is placed first, as in Fe O , and K Cl . In the formulæ of salts, it is likewise the *electro-positive* constituent or the basic oxide which is placed first, and not the acid. Thus the sulphate of potash is K O, S O_3 , and not $\text{S O}_3, \text{K O}$. Information respecting the constitution of a compound may often be expressed in its formula, by attending to this rule. Thus sulphuric acid of specific gravity 1.780, contains two proportions of water to one of acid, but by giving to it the following formula,



we express that one proportion only of water is combined as a base with the acid, and that the second proportion of water, the formula of which follows that of the acid, is in combination with this sulphate of water.

The above system of notation is complete, and sufficiently convenient for representing all binary compounds, and compounds belonging to the organic department of the science, in the formulæ of which the ultimate elements only are expressed. But when salts and double salts are expressed, the formulæ often become inconveniently long. They may often be greatly abbreviated, and made more distinct by expressing each equivalent of oxygen in an oxide or acid by a dot placed over the symbol of the other element, thus,

Protoxide of iron, $\dot{\text{Fe}}$

Sulphuric acid, $\ddot{\text{S}}$

Crystallized sulphate of protoxide of iron, $\dot{\text{Fe}} \ddot{\text{S}}, \dot{\text{H}} + 6\dot{\text{H}}$

Alum, $\dot{\text{K}} \ddot{\text{S}}, \text{Al} \ddot{\text{Al}} \ddot{\text{S}}_3 + 24\dot{\text{H}}$

Felspar, $\dot{\text{K}} \ddot{\text{Si}}, \text{Al} \ddot{\text{Al}} \ddot{\text{Si}}_3$

Oxalate of peroxide of iron and potash, $3\dot{\text{K}} \ddot{\text{C}}\ddot{\text{C}} + \dot{\text{Fe}}\dot{\text{Fe}}, 3\ddot{\text{C}}\ddot{\text{C}} + 6\dot{\text{H}}$

Such formulæ are more compact, and more easily compared with each other, the relation between the mineral felspar and alum without its water of crystallization, being seen at a glance on thus placing their formulæ together, the one having the symbol for silicon, the other that for sulphur, but everything else remaining the same. This abbreviated plan also exhibits more distinctly the relation between the equivalents of oxygen in the different constituents of a salt, which is always important.

It is to be observed, that the oxygen expressed by the dots placed over a letter is brought under the influence of the small figure attached to that letter, as for example, $\ddot{\text{S}}_3$ in the preceding formula of alum, means three proportions of sulphuric acid, so that this sign has the same value as if it were written $3\ddot{\text{S}}$.

Equivalents of *sulphur* are likewise sometimes expressed by commas placed over other symbols, as the trito-sulphuret of arsenic by $\overset{,,}{\text{As}}$, but such compounds are not of constant occurrence like the oxides, and do not create the same necessity for any new and arbitrary symbol. A compound body, such as cyanogen, which combines with a numerous series of other bodies is often for brevity expressed by the initial letter of its name, as

Cyanogen	.	Cy,
Benzoyle	.	Bz;

and the organic acids are sometimes expressed by a letter in the same way, but with the minus sign (—) placed over it, thus,

Acetic acid, by $\overline{\text{A}}$

Tartaric acid, by $\overline{\text{T}}$.

But arbitrary characters of this kind will always be explained, on the occasion of their introduction.

COMBINING PROPORTIONS.

All analyses prove that the composition of bodies is fixed and invariable : 100 parts of water are uniformly composed of 11.1 parts by weight of hydrogen, and 88.9 parts of oxygen, its constituents never varying either in nature or proportion. This and other substances may exist in an impure condition, from an admixture of foreign matter, but their own composition remains the same in all circumstances. It is this constancy in the composition of bodies which gives to chemical analyses all their value, and rewards the vast care necessarily bestowed upon their execution.

An examination of the composition of any class of bodies containing an element in common, such as the oxides, shows that any one element unites with very different quantities of the other elements. Thus in each of the five oxides, of which the composition is given below, the oxygen and other constituent appear in a different relation to each other.

Composition of Oxides.

Water.	Oxide of Copper.	Oxide of Zinc.	Oxide of Lead.	Oxide of Silver.
Oxygen . . 88.9	Oxygen . . 20.2	Oxygen . . 19.1	Oxygen . . 7.2	Oxygen . . 6.9
Hydrogen . . 11.1	Copper . . 79.8	Zinc . . 80.9	Lead . . 92.8	Silver . . 93.1
100	100	100	100	100

But the relation between the oxygen and the other constituent in these oxides will be seen more distinctly by stating their composition in such a way as to have the oxygen expressed by the same number in every case, or made equal to 100 parts. Thus,

Water.	Oxide of Copper.	Oxide of Zinc.	Oxide of Lead.	Oxide of Silver.
Oxygen . 100	Oxygen . 100	Oxygen . 100	Oxygen . 100	Oxygen . 100
Hydrogen . 12.5	Copper . 396	Zinc . 403	Lead . 1294	Silver . 1352
112.5	496	503	1394	1452

From which it follows, that

12.5 parts of hydrogen,
 396 parts of copper,
 403 parts of zinc,
 1294 parts of lead,
 1352 parts of silver,

combine with 100 parts of oxygen.

These numbers prove to be in some degree characteristic of the substances to which they are here attached, for when the composition of the *sulphurets* of the same substances is examined, it is found that exactly corresponding quantities of hydrogen, copper, &c. likewise combine with one and the same quantity of sulphur, although not with 100 parts of that element as of oxygen. The conclusion from an examination of the sulphurets is, that

12.5	parts of hydrogen,
396	parts of copper,
403	parts of zinc,
1294	parts of lead,
1352	parts of silver,

combine with 201 parts of sulphur. An examination of the *chlorides* of the same five elements likewise proves, that

12.5	parts of hydrogen,
396	parts of copper,
403	parts of zinc,
1294	parts of lead,
1352	parts of silver,

combine with 442 parts of chlorine. Hydrogen, copper, &c. are indeed found to unite in the proportions repeated in these tables with a certain or constant quantity of all other elements, as for example, with 978 *bromine*, with 1579 *iodine*, etc.

On extending the inquiry to other substances, it appears that for each of them, a number may be found which expresses in like manner, the proportion in which that substance unites with 100 parts of oxygen, 201 of sulphur, 442 of chlorine, &c. These numbers constitute the combining proportions, or equivalent quantities of bodies, which are introduced in the tables of the names of the elements at the beginning of this chapter, and which are the quantities understood to be expressed by the chemical symbols of these bodies. Any series of numbers may be chosen for the combining proportions, provided the true relation between them is preserved, as in the second series of numbers given in the same tables, which are all $12\frac{1}{2}$ times less than the numbers of the first series. The second series expresses particularly the proportional quantity of each of the elements, which unites with one part of hydrogen, the element, the combining proportion of which is the smallest,

and is on that account taken here as unity. But the other series which is the most convenient, being adopted, it may then be stated in general terms that *the combining proportion of a simple substance represents the quantity of that substance which combines with 100 parts of oxygen to form a protoxide.*

The first law of combination is, that bodies unite with each other in their combining proportions only, or in multiples of them, and in no intermediate proportions. This law may be illustrated by the compounds of nitrogen and oxygen, which are five in number, and are composed as follows :

Protoxide of nitrogen	.	.	Nitrogen 177, oxygen 100	.
Deutoxide of nitrogen	.	.	Nitrogen 177, oxygen 200	.
Nitrous acid	.	.	Nitrogen 177, oxygen 300	.
Peroxide of nitrogen	.	.	Nitrogen 177, oxygen 400	.
Nitric acid	.	.	Nitrogen 177, oxygen 500	.

The first compound consists of a single combining proportion of each of its constituents. But in the other compounds a single proportion of nitrogen is united with quantities of oxygen which correspond exactly with two, three, four and five combining proportions of that element. In the greater number of binary compounds, one of the constituents at least is present in the proportion of a single equivalent, like the nitrogen in this series, while the other constituent, generally the oxygen in oxides, and the electro-negative element in other compounds, is present in a multiple of its combining proportion. But the number of combining proportions which may enter into a compound, is subject to considerable variation as will appear from the following examples.

One proportion oxygen	+	One proportion	hydrogen, forms water.
Two proportions oxygen	+	One "	hydrogen, form peroxide of hydrogen.
One proportion oxygen	+	Two proportions	copper, forms suboxide of copper.
One " sulphur	+	Three "	oxygen, " sulphuric acid.
Two proportions sulphur	+	Two "	oxygen, form hyposulphurous acid.
Two " iron	+	Three "	oxygen, " peroxide of iron.
Two " sulphur	+	Five "	oxygen, " hyposulphuric acid.
Two " manganese	+	Seven "	oxygen, " hypermanganic acid.

Representing the constituents of a binary compound by A and B, the last being the oxygen or electro-negative constituent, the most frequent combination is $A+B$, then $A+2B$, $A+3B$, and $A+5B$. The combination of $2A+3B$, is not unfrequent, but $2A+B$, $A+4B$, $A+7B$, $2A+2B$, or $2A+5B$ are of com-

paratively rare occurrence. Combination between two elements is not known to occur in more complicated ratios than the preceding, if the compounds of carbon and hydrogen be excepted, which are numerous and exhibit great diversity of composition, like the compounds of organic chemistry generally, to which they properly belong.

Combination likewise takes place among bodies which are themselves compound, in proportional quantities, which are fixed, and determined by the law, that the combining number of a compound body is always the sum of the combining numbers of its constituents. Thus oil of vitriol, which is a combination of water and sulphuric acid, is composed of these bodies in the proportion of

Water	.	.	112.5
Sulphuric acid	.	.	501

in which the combining proportion of the water (112.5) is the sum of the proportions of its constituents; namely, of oxygen 100 and of hydrogen 12.5; and that of sulphuric acid (501), of those of sulphur 201 and of oxygen 300, there being three proportions of oxygen in sulphuric acid. The combining proportion of oxide of zinc is 503, the sum of oxygen 100 and zinc 403, and the compound of this oxide with sulphuric acid, or the salt, sulphate of zinc, consists of

Oxide of zinc	.	.	503
Sulphuric acid	.	.	501
			<hr/>
			1004

Of potash, the combining proportion is 590, or oxygen 100 added to potassium 490, and to this proportion of potash the usual proportion of sulphuric acid is attached in the sulphate of potash, which is composed of

Potash	.	.	590
Sulphuric acid	.	.	501
			<hr/>
			1091

Of these salts themselves, the combining proportions ought to be the sums obtained by the addition of the numbers of their constituents; and accordingly the double sulphate of zinc and potash consists of

Sulphate of zinc	.	1004
Sulphate of potash	.	1091
		<hr/>
		2095

Of nitric acid the constituents are one proportion of nitrogen 177, and five of oxygen 500, making together 677, which is the combining proportion of that acid, and is found to unite with 112.5 water, with 503 oxide of zinc, and with 590 potash, or with the same quantities of these oxides as combine with 501 sulphuric acid. Carbonic acid is composed of one proportion of carbon 76, and two proportions of oxygen 200, so that its combining number is 276, in which proportion it unites with 590 potash, to form the carbonate of potash. The equivalent quantities of all other acids and bases correspond in like manner with the numbers deducible from their composition. Indeed the law is found to hold in compounds of every class and character, and whether they contain few or many equivalents of their elements. Thus of the *vegeto-alkali morphia*, which contains a large number of equivalents, the combining proportion is the high number 3586, which is the sum of thirty-four proportions of carbon 2584, eighteen proportions of hydrogen 225, one proportion of nitrogen 177, and six proportions of oxygen 600; 3586 *morphia* being found to unite with 501 sulphuric acid, or a combining proportion of that acid, to form the sulphate of *morphia*.

Compound bodies likewise unite among themselves in multiples of their combining proportions, as well as in single equivalents. Thus 590 potash combine with 652 chromic acid, and with double that quantity, or 1304 chromic acid, to form the yellow and the red chromates of potash; the first containing one equivalent, and the second two equivalents of acid. The occurrence of multiple proportions was well illustrated by Dr. Wollaston in the carbonate and bicarbonate of potash. A quantity of the latter salt being divided into equal parts, one half was exposed to a red heat, by the effect of which the salt lost some carbonic acid and became neutral carbonate, and both portions being afterwards decomposed by an acid, the salt in its original condition was found to afford a measure of carbonic acid gas exactly the double of that yielded by the portion exposed to the high temperature. By experiments equally simple and convincing, he proved that in the three salts formed by oxalic acid and potash, the quantities of acid which combine with the same quantity of alkali are rigorously among themselves as the numbers 1, 2, and 4. The composition of all other super and sub salts is found to be in conformity with the same law, one of

the constituents being always present in the proportion of two or more equivalents.

The combining proportions of compound bodies depend entirely therefore upon those of their constituents, or upon the equivalents of the elementary bodies. The mode of determining these fundamental equivalents generally consists, as may be anticipated, in ascertaining the quantity of any element which exists united with 100 parts of oxygen in the protoxide of that element, which quantity is viewed as a single equivalent. Thus of hydrogen and lead, the protoxides are water and litharge, in which respectively 100 oxygen are associated with 12.5 hydrogen and 1294 lead, which numbers are therefore single equivalents of these elementary substances. But the difficulty still remains to know what is a protoxide; for the rule is not followed in all cases to consider that oxide of an element as the protoxide which contains the least proportion of oxygen. When only one oxide is known, it is presumed to be a protoxide and composed of single equivalents, unless it corresponds in properties with a higher degree of oxidation of some other element; and of several oxides of the same element that containing least oxygen is viewed as the protoxide, unless a higher oxide has better claims to be considered as such. Hence magnesia and oxide of zinc being the only oxides of magnesium and zinc known are protoxides; and water, litharge, potash, soda, lime, and protoxide of iron, which are all the lowest oxides of different metals, are admitted without objection to be protoxides, and become standards of comparison for this class of bodies; while alumina, the only oxide of aluminum, differing entirely from the protoxide of iron but closely resembling the peroxide of that metal, is considered a peroxide of similar constitution, or to contain three equivalents of oxygen and two of metal. Now in alumina 300 oxygen, or three equivalents, are united with 342 aluminum, one half of which number, or 171, is therefore the equivalent of aluminum. The true protoxide of aluminum, if it is capable of existing, still remains to be discovered. The first degree of oxidation of chromium, or the green oxide, is likewise a peroxide and not a protoxide, being analogous to alumina and the peroxide of iron. On the other hand the second degree of oxidation of copper, or the black oxide, and not the first degree of oxidation of that metal, must be viewed as the protoxide, or as composed of single equivalents, from its correspondence with the protoxide

of iron and a large class of admitted protoxides. The lower degree of oxidation of copper or the red oxide, which contains only half the proportion of oxygen in the black oxide, comes therefore to be considered a sub oxide, or a compound of two equivalents of metal and one of oxygen. For reasons somewhat similar the higher of the two grades of oxidation of mercury, or the red oxide of that metal, is now generally acknowledged to be the protoxide or to be composed of single equivalents, and the ash coloured oxide reputed a sub oxide. These sub-oxides of mercury and copper are capable of combining with acids, but they are the only sub-oxides which possess that property. It is the character of protoxides to form salts with acids; and of several oxides of the same metal, the protoxide is always the most powerful base.

Bodies likewise *replace* each other in combination, in equivalent quantities. Thus in the decomposition of water by chlorine, which occurs in certain circumstances, 442 parts of chlorine unite with 12.5 hydrogen or one equivalent of that body, to form hydrochloric acid, and displace at the same time and liberate 100 parts of oxygen. Hence the number 442 represents the combining proportion of chlorine which is equivalent in combination to, or can be substituted for 100 oxygen. Again in decomposing hydriodic acid, 442 chlorine unite with 12.5 hydrogen, and liberate 1580 iodine, which proportion of iodine may again acquire 12.5 hydrogen by decomposing sulphuretted hydrogen and set free 201 sulphur. Hence 1580 and 201 are the equivalent quantities of iodine and sulphur, which take the place of 442 chlorine or 100 oxygen in combination with 12.5 hydrogen. When 403 parts of zinc are introduced into a solution of nitrate of copper, they dissolve, acquiring 100 oxygen and 677 nitric acid, and become nitrate of zinc, while 396 parts of metallic copper are deposited, which had previously been in the state of nitrate and in combination with the above-mentioned quantities of oxygen and nitric acid, and the solution remains otherwise unaltered. Zinc throws down nearly all the metals from their solutions in acids in the same manner, and if the quantity of this substance introduced into the solutions and dissolved, be a combining proportion, as in the instance given, the quantities of the metals precipitated will also be combining proportions of those metals. The quantity of zinc employed may be varied, but the quantity of other metal

precipitated will still be to the quantity of zinc dissolved, in the ratio of the combining numbers of the two metals. Lead, copper, tin, or any other metal, when it acts like zinc as a precipitant, likewise throws down equivalent quantities of other metals, and takes their place in the pre-existing compound. The substitution in a saline compound of one metal for another, which thus occurs, without any change in the character of the compound, shows how justly the combining proportions of bodies are also termed their equivalent quantities or equivalents. The metal displaced, and that substituted for it, have evidently the same value in the construction of the compound, and are truly equivalent to each other.

The equivalent proportions of such oxides as are bases, are ascertained by finding what quantity of each saturates the known combining proportion of an acid. Thus to saturate 501 parts, or a combining proportion of sulphuric acid, the following proportions of different bases are requisite, and are equivalent in producing that effect :

Magnesia	258
Lime	356
Soda	391
Protoxide of manganese	445
Potash	590
Strontian	647
Barytes	956
Protoxide of lead	1394
Oxide of silver	1450

The addition of these bodies to sulphuric acid in the above proportions destroys its sour taste and other properties as an acid, of which the most characteristic is that of reddening certain vegetable blue colours, such as litmus. The acid is said to be neutralized or saturated, and the product or compound formed is a neutral salt which does not alter the blue colour of litmus. Of the bases mentioned, magnesia has the greatest saturating power, and oxide of silver the least; the proportion of these bases necessary to saturate the same quantity of sulphuric acid being 258 of the former, and 1450 of the latter.

Conversely the equivalent proportions of acids are the quantities which neutralize the known equivalent of any base or alkali. Thus 590 parts of potash, or a combining proportion is deprived of its alkaline properties, of which the most obvious

are its caustic taste and power to restore the blue colour of red-denied litmus, by the following proportions of different acids, and a neutral compound or salt produced in every case :

Sulphurous acid	.	.	.	401
Sulphuric acid	.	.	.	501
Hydrochloric acid	.	.	.	454.5
Nitric acid	.	.	.	677
Chloric acid	.	.	.	912
Hyperchloric acid	.	.	.	1142
Iodic acid	.	.	.	2078
Hyperiodic acid	.	.	.	2278

It thus appears that the acids differ as widely among themselves in their equivalent quantities as the bases do. The equivalent of either an acid or base thus deduced from its neutralizing power is always the same as that indicated by its composition, namely the sum of the equivalent numbers of its constituents. As the bases which saturate acids fully are all protoxides, it also necessarily follows that there are always 100 parts of oxygen contained in the proportion of base which neutralizes the equivalent of an acid.

The equivalents of both acids and bases are likewise observed in those decompositions in which one acid is substituted for another acid in combination, or one base for another base. Thus an equivalent of sulphuric acid is found to disengage the equivalent quantity exactly of sulphurous acid from the sulphite of soda, of nitric acid from the nitrate of potash or of hydrochloric acid from the chloride of sodium, and to replace it in combination with the base, forming in every case a neutral sulphate. An equivalent of potash separates in like manner an equivalent of magnesia, of lime, of barytes or of protoxide of lead from its combination with an acid. The proportion of acid or base necessary to produce a certain amount of decomposition may therefore be calculated from a knowledge of the equivalents of bodies, and such knowledge comes to be of the most frequent and valuable application for practical purposes.

But the substitution of equivalent quantities of different bodies for one another is most strikingly exhibited in the decompositions which follow the mixture of certain neutral salts. An equivalent of sulphate of magnesia being mixed with an equivalent of nitrate of barytes, the two bases exchange acids,

the original salts disappear completely and two new salts are produced, the sulphate of barytes which is insoluble and precipitates, and the nitrate of magnesia which remains in solution, as represented in the following diagram in which the equivalent quantities are expressed :

Before decomposition.			After decomposition.
759 sulphate	{ 258 magnesia	.	935 nitrate of
of magnesia	{ 501 sulphuric acid	.	magnesia.
1634 nitrate	{ 677 nitric acid	.	
of barytes	{ 957 barytes	.	1458 sulphate
			of barytes.

After a double decomposition of this kind, the liquid remains *neutral*, or there is no redundancy of either acid or base, because each of the new salts is composed of a single equivalent of acid and of base like the salts from which they are formed. If one of the salts be added in a larger proportion than its equivalent quantity the excess does not interfere with the decomposition, and remains itself unaffected, the decomposition proceeding no farther than the equivalents present. Hence the general observation that neutral salts continue neutral after decomposition, in whatever proportions they may be mixed.

But the modes of fixing the equivalent numbers which have been stated are inapplicable to several elementary bodies, such as nitrogen, phosphorus, carbon, boron, silicon and some metals, of which the protoxides are not bases and are uncertain. Nitrogen enters into nitric acid, of which acid it is known that the equivalent is 677, and that it contains five equivalents or 500 parts of oxygen, and consequently 177 parts of nitrogen. It is doubtful, however, whether 177 represents one or two equivalents of nitrogen. But the equivalent of ammonia likewise contains 177 nitrogen, and a less proportion is never found in the equivalent of any other compound into which that element enters. The number 177 is, therefore, *the least combining proportion* of nitrogen, and must on that account be taken as one equivalent. The equivalent of phosphorus can be shown on the same principle to be 392.28, that of arsenic 940.08 and that of antimony 1612.90, as given in the tables, and not the halves of these numbers as commonly estimated. These three bodies agree with nitrogen in their chemical relations, and the numbers recommended represent the quantities which replace

177 nitrogen in analogous compounds. The equivalent of carbon may be deduced from the known equivalent of its compound, carbonic acid. But the equivalents of boron and silicon cannot be fixed upon with the same certainty, owing to the doubt which hangs over the equivalents of boracic and silicic acids.

Of the facts which involve the principle of combination in definite and equivalent proportions the last mentioned appears to have been the first observed and explained. Wenzel of Freyberg in Saxony so far back as 1777 made an analysis of a great variety of salts with surprising accuracy, which enabled him to perceive that the neutrality which is observed after the mutual decomposition of neutral salts depends upon this, that the quantities of different acids which saturate an equal weight of one base will also saturate equal weights of any other base.

Richter of Berlin confirmed and extended the observations of Wenzel, attaching proportional numbers to the acids and bases, and remarking for the first time that the neutrality does not change during the precipitation of metals by each other, and also that the proportion of oxygen in the equivalents of bases is the same in all, and may be represented by 100 parts. But the first foundations of a complete system of equivalents, embracing both simple bodies and their compounds were laid by Dalton, at the same time that he announced his atomic theory.* The observation that the equivalent of a compound body is the sum of the equivalents of its constituents, and the discovery of combination in multiple proportions are peculiarly his. Dr. Wollaston afterwards adapted the more important equivalents to the common sliding rule of Gunter, by means of which, proportions can be observed without the trouble of calculation. This instrument, which is known under the name of *the scale of chemical equivalents*, contributed largely to the diffusion of the knowledge of the proportional numbers, but is not itself of much practical value.

The numerical accuracy of the equivalents assigned to bodies, depends entirely upon the exactness of the chemical analyses from which they are deduced. The generally received series of numbers, which is adopted in this work, was drawn up by Berzelius from data supplied in a great measure by himself.

* New system of Chemical Philosophy, 1807.

The consideration of the laws of Wenzel and Richter, which were long overlooked or misunderstood, was revived by him, and by a series of analytical researches unrivalled for their extent and accuracy he first impressed upon chemistry the character of a science of number and quantity, which is now its highest recommendation. Several of Berzelius's numbers received a valuable confirmation from Dr. Turner, whose inquiries were especially directed to test an hypothesis respecting them, advocated by some of his contemporaries; namely, that the equivalents of all the elements are multiples of the equivalent of hydrogen, and consequently if that equivalent be made equal to 1, all the others will be whole numbers. Dr. Turner's results are incompatible with such a relation among the equivalent numbers, the existence of which indeed is disproved by all accurate analyses.*

Still the existence of a simple relation between certain equivalents has been pointed out by M. Dumas; and it is possible that the numbers of each of the pairs below, which approach so closely, would actually coincide, as they do in one pair, were they determined with absolute accuracy.

Cobalt	368.99	Platinum	1233.5
Nickel	369.68	Iridium	1233.5
Osmium	1244.49	Sulphur	201.17
$\frac{1}{2}$ Eq. Gold	1243.01	$\frac{1}{4}$ Eq. Tellurium.	200.44

But these are the only equivalents between which there are good grounds for supposing that any relation exists. The identity of the atomic weights of platinum and iridium is the most certain, having been experimentally confirmed by Berzelius since it was first asserted by Dumas.

Of the two series of numbers given in the tables, the first in which oxygen is made equal to 100, and which is called the oxygen series, is the most convenient, and will alone be made use of in the following pages. The numbers of this series are so large that the fractional portion may, I believe, be safely neglected in computing by them, being within the unavoidable errors of observation in chemical analyses, and the nearest whole number may be adopted, except in the following equivalents, although even in them it is unnecessary to go beyond the first decimal figure :

* Philosophical Transactions, 1833, p. 523.

Hydrogen	.	.	12.5
Carbon	.	.	76.4
Chlorine	.	.	442.6
Lead	.	.	1294.5

The numbers belonging to the other or hydrogen series, are all twelve and a half times less than the corresponding numbers of the oxygen series, into which the former may most easily be converted by multiplying them by one hundred, and dividing the product by eight. Or the numbers of the oxygen may be reduced to the hydrogen scale, which many prefer, by dividing them by one hundred, and multiplying the quotient by eight. The numbers of the hydrogen scale are of a lower term, smaller and more easily recollected than the oxygen series, but their fractional portion can seldom be neglected in computing by means of them, and the insecurity of the basis on which this series rests is a great objection to its adoption. There is an actual experimental difficulty in determining the equivalent of hydrogen with precision, arising from its extreme smallness; so that this equivalent itself is more liable to correction and alteration than most others, which would necessitate a corresponding change throughout the whole scale.

ATOMIC THEORY.

The laws of combination and the doctrine of equivalents which have just been considered, are founded upon experimental evidence only, and involve no hypothesis. The most general of these laws were not however suggested by observation, but by a theory of the atomic constitution of bodies, in which they are included, and which affords a luminous explanation of them. The partial verification which this theory has received in the establishment of these laws, adds greatly to its interest, and is a strong argument in favour of its truth. It is the atomic theory of Dalton, the essential part of which may be stated in a few words.

Although matter appears to be divided and comminuted in many circumstances to an extent beyond our powers of conception, it is possible that it may not be indefinitely divisible; that there may be a limit to the successive division or secability of its parts, a limit which it may be difficult or impossible to reach by experiment, but which nevertheless exists. Matter may

therefore be composed of ultimate particles or atoms, which are not farther divisible, and each of which possesses a certain absolute and possibly appreciable weight. Now the question arises, is the atom in every kind of matter of the same weight, or do atoms of different kinds of matter differ in weight? Are the ultimate particles, for instance, to which charcoal and sulphur are reducible, of the same or of different weights? Let their weights be supposed to be different, to be in the proportion of the equivalent numbers of sulphur and charcoal, which thus become *atomic weights*, and so of the atoms of other elementary bodies, and the whole laws of combination follow by the simplest reasoning. The atoms of the elementary bodies may be represented to the eye by spheres or by circles in which their symbols are inscribed to distinguish them, as in the following examples, with their relative weights.

Name.	Atom.	Weight of atom.
Oxygen. . . .	(O)	100
Hydrogen . . .	(H)	12.5
Nitrogen. . . .	(N)	177
Carbon.	(C)	76.4
Sulphur	(S)	201
Lead.	(Pb)	1294.5

Chemical combination takes place between the atoms of bodies, which then come into juxtaposition; and in decomposition the simple atoms separate again from each other, in possession of their original properties. The atom or integrant particle of a compound body is an aggregation of simple atoms, and must therefore have a weight equal to the sum of their weights, as will be obvious from the exhibition of the atomic constitution of a few compounds.

	Atom.	Weight.
Water (oxide of hydrogen)	(H)(O)	12.5 + 100 = 112.5
Protoxide of nitrogen. .	(N)(O)	177 + 100 = 277
Deutoxide of nitrogen. .	(N)(O)(O)	177 + 200 = 377
Sulphuric acid.	(S)(O)(O)(O)	201 + 300 = 501
Oxide of lead.	(Pb)(O)	1294.5 + 100 = 1394.5
Sulphate of lead.	{ (Pb)(O) } { (S)(O)(O)(O) }	1394.5 + 500 = 1895.5

It is unnecessary to make any assumption as to the nature,

size, form, or even actual weight of the atoms of elementary bodies, or as to the mode in which they are grouped or arranged in compounds. All that is known or likely ever to be known respecting them is their relative weight. The atom of oxygen is eight times heavier than that of hydrogen, or they are to each other as 100 to 12.5, but their actual weights are undetermined. To afford the means of expressing the relative weights of these and other atoms, a number which is entirely arbitrary is assigned to one of them, namely 100 to the atom of oxygen, and then the weight of the atom of hydrogen can be said to be 12.5, of nitrogen 17.7, of carbon 76.4, of sulphur 201, and of lead 1294.5. A single atom of water contains one atom of oxygen, (100) and one of hydrogen, (12.5) and must therefore weigh 112.5; an atom of oxide of lead contains one atom of oxygen and one of lead, which weigh together 1394.5; an atom of sulphuric acid, one atom of sulphur and three atoms of oxygen, which weigh together 501; and an atom of sulphate of lead, including one of each of the preceding compound atoms must weigh $1294.5 + 501$, or 1795.5.

The equivalent quantities being now represented by atoms, it necessarily follows that bodies can combine in these quantities or multiples of them only, and not in intermediate proportions, for atoms do not admit of division. In a series of several compounds of the same elements, such as the oxides of nitrogen, which was formerly referred to in illustration of combination in multiple proportions, (page 109) one atom of nitrogen combines with one, two, three, four and five atoms of oxygen, and a simple ratio between the quantities of oxygen in these compounds is the consequence. The equivalent of a compound body also is the sum of the equivalents of its constituents, for the weight of a compound atom is the weight of its constituent atoms.

By the juxtaposition, separation, and exchange of one atom for another in compounds, all kinds of combination and decomposition in equivalent quantities may be produced, while the substitution of ponderable masses for the abstract idea of equivalents renders the whole changes most readily conceivable.

This theory being adopted as a useful, while it is at the same time, a highly probable representation of the laws of combination, its terms atom and atomic weight may be used as synonymous with equivalent, equivalent quantity and combining proportion.

M. Dumas is disposed to modify the atomic theory so far as to allow the divisibility of the atoms or ultimate masses in which a body enters into combination, and to suppose that they are groups of more minute atoms, into which they may be divided by physical, but not by chemical forces. He distinguishes the atoms which correspond with equivalents as *chemical atoms*, and allowing them to represent truly and constantly the least quantities in which bodies combine, still supposes that under the influence of heat and perhaps other physical agencies, these molecules may be subdivided into atoms of an inferior order, of which for example, two, four or a thousand are included in a single chemical atom.* But surely such a view is entirely subversive of the atomic theory. It is principally founded on the assumed existence of a similarity between atoms in their capacity for heat, and in their volume while in the gaseous state, in which it would be more natural to admit a difference among different atoms.

SPECIFIC HEAT OF ATOMS.

The quantity of heat necessary to raise the temperature of equal weights of different bodies a single degree, varies according to their nature, and may be expressed by numbers which are the capacities for heat or specific heats of these bodies (page 22). This difference appears in the numbers for several simple bodies placed together in the first column of the table below, among which no relation can be perceived. But if the comparison is made between the capacity for heat not of *equal* weights, but of *atomic* weights or equivalent quantities of the same bodies, as in the second and third columns of the table, then the numbers for several bodies are found to be nearly the same, and those of others to bear a simple relation to each other.

* Leçons sur la Philosophie Chimique, professées au Collège de France, par M. Dumas, page 233. Paris, 1837.

SPECIFIC HEAT

	I.	II.	III.	IV.
	Of equal weights.	Of atoms.	Of atoms.	Atomic weights.
	Specific heat of same weight of water being 1.	Specific heat of atom of water being 1.	Specific heat of atom of lead being 1.	
Lead . .	0.0293	0.3372	1.0000	1294.5
Tin . .	0.0514	0.3358	0.9960	735
Zinc . .	0.0927	0.3321	0.9850	403
Copper . .	0.0949	0.3340	0.9908	396
Nickel . .	0.1035	0.3404	1.0095	370
Iron . .	0.1100	0.3315	0.9831	339
Platinum . .	0.0314	0.3443	1.0211	1234
Sulphur . .	0.1380	0.3359	0.9963	201
Mercury . .	0.0330	0.3714	1.1015	1266
Tellurium . .	0.0912	0.6501	1.9283	802
Arsenic . .	0.081	0.6768	2.0074	940
Silver . .	0.0557	0.6694	1.9855	1352
Gold . .	0.0298	0.6585	1.9531	2486
Phosphorus . .	0.385	1.3415	3.9789	392
Iodine . .	0.089	1.2500	3.7074	1580
Cobalt . .	0.1498	0.4914	1.4574	369
Carbon . .	0.25	0.1698	0.5036	76.4
Bismuth . .	0.0288	0.2271	0.6736	887

Of the first nine substances which are all metals, with the exception of sulphur, the capacities of the atoms approach so closely, that they may be considered as identical; their capacities appearing to be all nearly one-third of that of the atom of water, in the second column; and nearly coinciding with the capacity of the atom of lead, one of their number in the third column. The weights of the atoms themselves are added in a fourth column, for convenience of reference. The nine substances in question, taken in the proportions of their atomic weights, will, therefore, undergo an equal change of temperature on assuming an equal quantity of heat. The four metals which follow in the table, namely, tellurium, arsenic, silver and gold, appear to have an equal capacity for heat, which is double that of lead and the class which coincides with it, while the capacity of phosphorus and iodine is four times greater than that of lead and its class. The capacity of the atom of

cobalt appears to be once and a half, and that of the atom of carbon to be one-half of that of lead. But bismuth appears to have no clear relation to the others, the capacity of its atom being 0.6736, referred to that of lead as 1. The general results, therefore, may be stated as follows :

Specific heat of atom of lead			.	.	1
"	"	tin	.	.	1
"	"	zinc	.	.	1
"	"	copper	.	.	1
"	"	nickel	.	.	1
"	"	iron	.	.	1
"	"	platinum	.	.	1
"	"	sulphur	.	.	1
"	"	mercury	.	.	1
"	"	tellurium	.	.	2
"	"	arsenic	.	.	2
"	"	silver	.	.	2
"	"	gold	.	.	2
"	"	phosphorus	.	.	4
"	"	iodine	.	.	4
"	"	cobalt	.	.	$1\frac{1}{2}$
"	"	carbon	.	.	$\frac{1}{2}$

Messrs. Dulong and Petit, whose researches supplied these valuable results, drew a more general conclusion from them, namely that all atoms, or at least all simple atoms, have the same capacity for heat, and that those atomic weights which are inconsistent with that supposition, ought to be altered and accommodated to it. The specific heat of a body would thus afford the means of fixing its atomic weight. Some of the alterations in the atomic weights, which would follow the adoption of this law, might be advocated upon other grounds, such as halving the atomic weights of silver and gold, but certain other changes equally inevitable are wholly inadmissible; such as dividing the atom of tellurium by two, or reducing it from 802 to 401, although the most perfect analogy subsists between tellurium and sulphur in their compounds, in all of which 802 parts tellurium, and not 401, replace 201 sulphur or one equivalent. The equivalent of phosphorus would require to be divided by four, while that of arsenic, which it so closely represents in compounds, is divided only by two. Of the admitted equivalents of nickel and cobalt also, which replace each

other in analogous compounds, the first remains unaltered, while the last must be reduced to two-thirds of its present amount.

It must be concluded then, that elementary atoms have not necessarily the same capacity for heat, although a simple relation appears always to exist between their capacities. The capacities of the three gaseous elements, oxygen, hydrogen and nitrogen, may likewise be adduced in support of such a relation, provided they are the same for equal volumes of the gases, agreeably to the observations of Dulong. But this relation can only be looked for between bodies while under the same physical condition, and perhaps agreeing in other circumstances also, for the capacity for heat of the same body is known to vary under the different forms of solid, liquid and gas; and, indeed, while the body is in the same state, its capacity appears not to be absolutely constant, but to increase perceptibly at elevated temperatures (page 23).

The capacities of compound atoms have not been submitted to a sufficiently extensive examination to determine whether equally simple relations subsist generally among them. In two classes of analogous combinations, however, the capacities of the atoms for heat have been found by M. Neumann to approach so closely, that they may be admitted to be the same, the differences being sufficiently accounted for by the errors of observation unavoidable in such delicate researches.

	Of equal weights. Specific heat of same weight of water being 1.	Of atomic weights. Specific heat of atom of water being 1.
Carbonate of lime . . .	0.2044	0.1148
Carbonate of barytes . . .	0.1080	0.1181
Carbonate of iron . . .	0.1819	0.1156
Carbonate of lead . . .	0.0810	0.1200
Carbonate of zinc . . .	0.1712	0.1187
Carbonate of strontian . .	0.1445	0.1184
Dolomite (carbonates of lime and magnesia) . . .	0.2111	0.1121
Mean		0.1168

A small class of sulphates presented a similar result:

	Of equal weights.	Of atomic weights
Sulphate of barytes . . .	0.1068	0.1384

Sulphate of lime	.	.	0.1854	.	0.1412
Sulphate of strontian	.	.	0.1300	.	0.1326
Sulphate of lead	.	.	0.0830	.	0.1398
					<hr/>
Mean					0.1380

The numbers in the second column of both tables, deviate very little from their mean, but there is no relation between the two means. Identity in capacity for heat is, therefore, to be looked for in compound atoms of the same nature, and which closely agree in their chemical relations, like the numbers of each group, but not between compound atoms which are differently constituted.

RELATION BETWEEN THE ATOMIC WEIGHTS AND VOLUMES OF BODIES IN THE GASEOUS STATE.

Several of the elementary bodies are gases, such as oxygen, hydrogen, nitrogen and chlorine, and the proportions in which they combine can be determined by *measure* with equal, if not greater facility than by weight. A relation of the simplest nature is always found to subsist between the measures or volumes in which any two of the gaseous elementary bodies unite. This arises from the circumstance that the specific gravities of gases either correspond exactly with their atomic weights, or bear a simple relation to them. The atom of chlorine is $35\frac{1}{2}$ times heavier than that of hydrogen; and chlorine gas is also $35\frac{1}{2}$ times heavier than hydrogen gas, so that the combining measures of these two gases, which correspond with single equivalents, are necessarily equal. The atom of nitrogen, and its weight as a gas being both 14.2 times greater than the atom and weight of hydrogen gas, their combining volumes must be the same. The atom of oxygen is eight times heavier than that of hydrogen, but oxygen gas is sixteen times heavier than hydrogen gas, so that taken in equal volumes these two gases are in the proportion by weight of two equivalents of oxygen to one of hydrogen. Hence, in the combination of single equivalents of these elements to form water, half a volume or measure of oxygen gas unites with a whole volume or measure of hydrogen gas. One volume of nitrogen, also unites with half a volume of oxygen, and with a whole volume of the same gas, to form respectively the protoxide and deutoxide of nitrogen.

The exact ratio of one to two in which oxygen and hydrogen

gases combine by measure, was first observed by Humboldt and Gay-Lussac in 1805. The subject was pursued by the latter chemist, who established the simple ratios in which gases generally combine, and published the laws observed by him, or his Theory of Volumes, shortly after the announcement of the Atomic Theory by Dalton. They afforded new and independent evidence of the combination of bodies in definite and also in multiple proportions, equally convincing as the observed proportions by weight in which bodies unite. Gay-Lussac likewise observed that the product of the union of two gases, if itself a gas, sometimes retains the original volume of its constituents, no contraction or change of volume resulting from their combination; thus one volume of nitrogen and one volume of oxygen form two volumes of deutoxide of nitrogen; one volume of chlorine and one volume of hydrogen form two volumes of hydrochloric acid gas; and that when contraction follows combination, which is the most common case, the volume of the compound gas always bears a simple ratio to the volumes of its elements. Thus two volumes of hydrogen and one of oxygen form two volumes of steam, one volume of nitrogen and three of hydrogen gas form two volumes of ammoniacal gas, one volume of hydrogen and one-sixth of a volume of sulphur-vapour form one volume of sulphuretted hydrogen gas. In these and all other statements respecting volumes, the gases compared are supposed to be in the same circumstances as to pressure and temperature.

The uniformity of properties observed among gases in compressibility and dilatibility by heat, has appeared to many chemists to indicate a similarity of constitution, and to favour the idea that they all contain the same number of atoms in the same volume. May not equal volumes of oxygen and hydrogen gases, for instance, be represented by an equal number of atoms of oxygen and hydrogen respectively placed at equal distances from each other, and the difference of sixteen to one in the densities of the two gases arise from the atom of oxygen being really sixteen times heavier than that of hydrogen? Equal volumes of gases would then contain an equal number of atoms, and one, two or three volumes would be an equivalent expression to one, two or three atomic proportions, the terms *volume* and *atom* becoming of the same import, or expressing equal quantities of bodies. But such a view is

obviously inapplicable to compound gases, as their volume has a variable relation to that of their elements; and its adoption would require grave alterations to be made in the atomic weights of several of the elements themselves, to accommodate these weights to the observed densities of the bodies in the gaseous state. This will be seen from the following table, in which the volume or fractional part of a volume placed against each element always contains the same number of its presently received atoms. These volumes are, therefore, the equivalent volumes of the elements, and may be viewed as representing the bulk of their atoms in the gaseous state, *the combining volume of hydrogen being here taken as one.*

ATOMS						
			Volume.		Weight.	
Hydrogen	.	.	1	.	.	12.5
Nitrogen	.	.	1	.	.	177
Chlorine	.	.	1	.	.	442.6
Bromine	.	.	1	.	.	978
Iodine	.	.	1	.	.	1580
Oxygen	.	.	$\frac{1}{2}$.	.	100
Phosphorus	.	.	$\frac{1}{2}$.	.	392
Arsenic	.	.	$\frac{1}{2}$.	.	940
Sulphur	.	.	$\frac{1}{6}$.	.	201
Mercury	.	.	2	.	.	1266

Of the first five bodies enumerated, equivalent weights occupy equal volumes. It was indeed the observation of this equality between the atom and volume in these gases, that led to the supposition of that relation being general. But the atoms of oxygen, phosphorus and arsenic occupy only half a volume, and would require to be doubled to fill the same volume as the preceding class. The present atom of sulphur affords only one-sixth of a volume of vapour, and must, therefore, be multiplied by six to afford a whole volume; while the atom of mercury supplies two volumes of vapour, and would, therefore, require to be divided by two, or reduced to one-half of its present number. Of these changes the required modification of the atoms of phosphorus, arsenic and sulphur is incompatible with their chemical relations to other bodies which are best established, and is quite inadmissible. The densities of the vapours of these bodies must, therefore,

be viewed as decisive against the equality of the equivalent volumes of the elementary gases. A volume of sulphur vapour must be allowed to contain three times as many atoms as an equal volume of oxygen gas, six times more than the same volume of hydrogen gas, and twelve times more than the same volume of mercury vapour. A similar constitution cannot be assigned to these vapours, unless on the assumption of Dumas, that chemical atoms of the same kind may group together, and form larger compound atoms or molecules, or divide into smaller molecules. The molecule of hydrogen in the gaseous state being the same as its chemical atom, each molecule of oxygen while in the state of gas would be an aggregate of two chemical atoms, and each of sulphur of six; while mercury must suffer molecular division in the state of vapour, each of its chemical atoms being parted into two, in order that equal volumes of these different gases and vapours should contain the same number of molecules or atoms. But such views are entirely speculative.

In the farther consideration of the proportions in which gases combine by measure, it will be found conducive to perspicuity to adopt the combining volume of oxygen as the unit (instead of that of hydrogen as in the last table), in terms of which to express the combining measures of other gases, both simple and compound. The combining measure of oxygen being one volume, *the combining measure* of hydrogen and its class will be *two volumes*; or the atom of oxygen gives one and the atom of hydrogen two volumes of gas. Volumes of the gases may be represented by equal squares with their relative weights inscribed, the numbers having reference to the number assigned to the oxygen volume. If that number be 100, or the atomic weight of oxygen, as in column I of the table below, then the number to be inscribed in each of the two volumes forming the combining measure of hydrogen will be 6.25 or half its atomic weight, the combining measure itself having the full atomic weight of hydrogen, namely 12.5; and so of other gases, the combining measure has the whole atomic weight which is divided among the component volumes. But there is the reason for preferring the number 1102.6 to 100 for the standard oxygen volume, that the weight of a volume of *air* being taken as 1000, that of an equal volume of oxygen is 1102.6; and consequently the corresponding number for the volume of hydrogen, 69,

expresses the relation in weight of that gas also to air, and so do the corresponding numbers for all the other gases. The numbers on this scale, which express the relative densities of a volume of each gas, and are inscribed in the squares of column II, are indeed the common *specific gravities of the gases*.

I.		II.	
Atomic weight.	Combining measure.	Combining measure.	
		Air . .	1000
Oxygen 100	100	1102.6
Phosphorus . . . 392	392	4327
	6.25		69
Hydrogen . . . 12.5	6.25	69
	221.3		2470
Chlorine . . . 442.6	221.3	2470
	316.25 : 316.25		6969 : 6969
Mercury . . . 1266	316.25 : 316.25	6969 : 6969

The double squares which represent the combining measures of hydrogen and chlorine are divided into volumes by *dotted* lines, to shew that the division is imaginary, the partition of a combining measure, like that of an atom which it represents, being impossible. The specific gravities of gases being merely the relative weights of equal volumes, may be expressed by the numbers in the squares of the first column; and the specific gravity of oxygen being accordingly made 100, the specific gravity of any other gas will either be the same number as its atomic weight or an aliquot part of it. Or if the specific gra-

vity of oxygen be made 1 or 1000, the relation of densities to atomic weights will still be very obvious.

The combining measures of *compound* gases, although variable, have still a constant and a simple relation to each other, such as 1 to 1, 1 to 2, or 2 to 3; their elements in combining suffering either no condensation or a definite and very simple change of volume. Hence the density of a compound gas may often be calculated with more precision from the densities of its constituents and a knowledge of the change of volume, if any, which occurred in combination, than it can be determined by experiment.

To deduce on this principle the specific gravity of steam. It consists of single equivalents of oxygen and hydrogen, of which the combining measure of the first is one, and that of the second two volumes. These *three* volumes, weigh $1102.6 + 69 + 69 = 1240.6$, and they form *two* volumes of steam; of which one volume must, therefore, weigh 1240.6 divided by two, or 620.3, which is, consequently, the calculated specific gravity of steam, referred to that of air as 1000. The relations in volume of the gases before and after combination may be thus exhibited.

Combining measure, or
one volume of oxygen.

Combining measure, or
two volumes of hydrogen.

Combining measure, or
two volumes of steam.

1102.6		69		620.3
	
		69	=	620.3
1240.6				1240.6

It thus appears necessary to inscribe 620.3 in each volume of steam, to make up 1240.6, the known weight of the two volumes.

In the formation of the hydrochloric acid, equal measures of chlorine and hydrogen unite without condensation, so that the product possesses the united volumes of its constituent gases.

Combining measure
of hydrogen or two
volumes.

Combining measure
of chlorine or two
volumes.

Combining measure of
hydrochloric acid or four
volumes.

69		2470		1269.5	1269.5
.....	=
69	+	2470		1269.5	1269.5
5078				5078	

The specific gravity or weight of a single volume of hydrochloric acid is, therefore, obtained by dividing 5078 by 4, and is 1269.5.

The specific gravity of the vapour of an elementary body, which there are no means of ascertaining experimentally, may sometimes be calculated from the known density of a gaseous compound containing it. The density of carbon vapour may be thus deduced from the observed density of carbonic oxide gas. Assuming that the combining measure of carbon is double that of oxygen, as is true of hydrogen and several other elementary bodies, then carbonic oxide, which like water consists of single equivalents of its constituents, will resemble steam in its constitution also, and be composed of one volume of oxygen gas and two volumes of carbon vapour condensed into two volumes. The weight of a single volume of carbonic oxide being 972.7, two volumes (1945.4) may be resolved, as shewn in the diagram below, into one volume of oxygen, 1102.6, and two volumes of carbon-vapour, 842.6, ($1945.4 - 1102.6 = 842.6$) each of which it follows must weigh 421.3.

Combining measure or two volumes of carbonic oxide.	Combining measure or one volume of oxygen.	Combining measure or two volumes of carbon vapour.
<div style="border: 1px solid black; padding: 5px; display: inline-block;"> 972.7 972.7 </div>	<div style="border: 1px solid black; padding: 5px; display: inline-block;">1102.6</div>	<div style="border: 1px solid black; padding: 5px; display: inline-block;"> 421.3 421.3 </div>
1945.4	=	1945.4

But the density 421.3 thus assigned to carbon vapour will only be true, if it corresponds with hydrogen in its combining measure; but the combining measure of carbon vapour may as well be one-half that of hydrogen, like that of phosphorus, or one-sixth like that of sulphur, and then the density will be double or six times that supposed. The important conclusion, however, that the density of carbon vapour is either 421.3, or some multiple or sub-multiple of that number is quite certain.

The two following tables comprise nearly all the accurate information which chemists at present possess respecting the specific gravities of gaseous bodies. The bodies placed in the first table are generally considered as belonging to the inorganic and those in the second, to the organic department of the science.

TABLE I.

GASES AND VAPOURS.	DENSITY.	ATOM.	
	Air=1000.	Volumes in combining measure.	Weight.
Oxygen	1102.6	1	100
Phosphorus.....	4327	1	392.28
Arsenic	10362	1	940.08
Arsenious acid.....	13670	1	1240.08
Sulphuret of mercury.. .	5384	$\frac{2}{3}$	1466.99
Sulphur	6648	$\frac{1}{8}$	201.17
Hydrogen	69	2	12.50
Nitrogen.....	976	2	177.04
Carbon (hypothetical)	421.5	2	76.44
Chlorine	2470	2	442.65
Iodine	8701	2	1579.50
Bromine	5393	2	978.31
Water	620.2	2	112.50
Protoxide of nitrogen	1527.3	2	277.04
Carbonic oxide	972.8	2	176.44
Carbonic acid	1524.1	2	276.44
Sulphurous acid	2210.6	2	401.17
Sulphuric acid (anhydrous)	2761.9	2	501.17
Sulphuretted hydrogen ..	1177	2	213.67
Light carburetted hydrogen	559.5	2	101.46
Cyanogen	1819	2	329.92
Mercury	6969	4	1265.82
Deutoxide of nitrogen	1039.3	4	377.04
Hydrochloric acid	1269.5	4	455.15
Hydriodic acid	4385	4	1592.00
Hydrobromic acid	2731	4	990.81
Hydrocyanic acid	944	4	342.42
Ammonia	591.5	4	214.54
Arsenuretted hydrogen	2695	4	952.58
Terchloride of arsenic.....	6295	4	2268.03
Teriodide of arsenic	15640	4	5678.58
Subchloride of mercury ...	8204	4	2974.29
Chloride of mercury	9439	4	1708.47
Subbromide of mercury	9665	4	3509.95
Bromide of mercury	12362	4	2244.13
Iodide of mercury (red)	15670	4	2845.32

TABLE II.

GASES AND VAPOURS.	FORMULA.	DENSITY. Air=1000.		Volumes in combin. measure.	OBSERVER.
		Calculated	Observed		
Ether	C_4H_5O	2583	2586	2	Gay-Lussac.
Methylic ether.	C_2H_3O	1601	1617	2	Dumas and Peligot.
Sulphate of methylene	C_2H_3O, SO_3	4369	4565	2	Idem.
Oxalic ether.	C_2H_5O, C_2O_3	5081	5087	2	Dumas and Boullay.
Succinic ether	$C_4H_5O, C_4H_2O_3$	6201	6220	2	Felix d'Arcet.
Oenanthic ether	$C_4H_5O, C_{14}H_{13}O_2$	10477	10508	2	Liebig and Pelouze.
Alkarsine	C_4H_6As	7281	7184	2	Bunsen.
Acetic acid	$C_4H_4O_2$	2778	2770	3	Dumas.
Methylene	C_2H_2	490	.	4	Dumas and Peligot.
Olefiant gas.	C_4H_4	981	985	4	M. de Saussure.
Gas from oil	C_8H_8	1962	1892	4	Faraday.
Oleene	$C_{12}H_{12}$	2942	2875	4	Fremy.
Elaene	$C_{18}H_{18}$	4156	4071	4	Idem.
Cetene	$C_{32}H_{32}$	7846	8007	4	Dumas and Peligot.
Benzin	$C_{12}H_6$	2736	2770	4	Mitscherlich.
Retinaphtha.	$C_{14}H_8$	3226	3230	4	Pelletier and Walter.
Retinyle.	$C_{18}H_{12}$	4247	4242	4	Idem.
Retinole	$C_{32}H_{16}$	7290	7110	4	Idem.
Naphthaline.	$C_{20}H_8$	4488	4528	4	Dumas.
Paranaphthaline	$C_{30}H_{12}$	6732	6741	4	Dumas and Laurent.
Camphene or oil of turpentine	$C_{20}H_{16}$	4763	4765	4	Dumas.
Camphor ..	$C_{20}H_{16}O_2$	5314	5468	4	Idem.
Menthene (from oil of mint)	$C_{20}H_{18}$	4830	4940	4	Walter.
Concrete essence of mint. .	$C_{20}H_{20}O_2$	5450	5620	4	Idem.
Wood-spirit.	$C_2H_4O_2$	1110	1120	4	Dumas and Peligot.
Hydrochlorate of methylene.	C_2H_3Cl	1738	1731	4	Idem.
Hydrofluatate of methylene. .	C_2H_3F	1169	1186	4	Idem.
Hydriodate of methylene. .	C_2H_3I	4882	4883	4	Idem.
Nitrate of methylene	C_2H_3O, NO_5	2640	2653	4	Idem.
Formate of methylene.	C_2H_3O, C_2HO_3	2083	2084	4	Idem.
Acetate of methylene.	$C_2H_3O, C_4H_3O_3$	2573	2563	4	Idem.
Alcohol	$C_4H_6O_2$	1601	1613	4	Gay-Lussac.
Mercaptan	$C_4H_6S_2$	2158	2326	4	Bunsen.
Hydrochloric ether.	C_4H_5Cl	2229	2219	4	Thénard.
Hydriodic ether	C_4H_5I	5321	5475	4	Gay-Lussac.
Nitrous ether	C_4H_5O, NO_3	2606	2626	4	Dumas and Boullay
Chlorocarbonic ether	C_4H_5O, C_2O_3Cl	3759	3829	4	Dumas.
Acetic ether	$C_4H_5O, C_4H_3O_3$	3066	3067	4	Idem.
Benzoic ether	$C_4H_5O, C_{14}H_3O_3$	5240	5409	4	Idem.
Pyromucic ether	$C_4H_5O, C_{10}H_3O_5$	4878	4859	4	Malaguti.
Chloride of aldehydene	C_4H_3Cl	2166	.	4	Liebig and Pelouze.
Oil of olefiant gas.	C_4H_3Cl, HCl	3407	3443	4	Gay-Lussac & Dumas
Bromide of aldehydene	C_4H_3Br	3642	3691	4	Regnault.
Hydrocarburet of bromine. .	C_4H_3Br, HBr	6373	6485	4	Idem.
Chloral.	$C_4HCl_3O_2$	5060	5130	4	Dumas.
Choloroform	C_4HCl_3	4113	4199	4	Idem.
Urethane	$C_6NH_7O_4$	3140	3096	4	Idem.
Oil of the ardent spirits from potatoes	$C_{10}H_{12}O_2$	3072	3147	4	Idem.
Aldehyde.	$C_4H_4O_2$	1531	1532	4	Liebig.
Acetone	$C_6H_6O_2$	2020	2019	4	Dumas.
Benzoic acid	$C_{14}H_6O_4$	4260	4270	4	Dumas & Mitscherlich
Eugenic acid ..	$C_{20}H_{12}O_5$	6000	6400	4	Dumas.
Formethylal.	$C_8H_{10}O_6$	2456	2500	6	Dumas.

From these tables, it appears that a simple relation always subsists between the combining measures of different bodies in the gaseous state :

That the combining measure of a few bodies is the same as that of oxygen, or *one volume* ; of a large number, double that of oxygen, or *two volumes* ; and of a still larger number, four times that of oxygen, or *four volumes* ; while combining measures of other numbers of volumes, such as *three* and *six*, or of fractional portions of one volume, such as *one-third*, are comparatively rare ;

That the specific gravity of a gas may be calculated from its atomic weight, or the atomic weight from the specific gravity, as they are necessarily related to each other. Thus, to find the specific gravity of a vapour like that of phosphorus, of which the combining measure is one volume, or the same as that of oxygen. The specific gravities of two bodies, of which the *volumes* of the atoms are the same, must obviously be as the *weights* of these atoms. Hence, 100 and 392.28 being the atomic weights of oxygen and phosphorus, and 1102.6, the known specific gravity of oxygen, the specific gravity of phosphorus vapour is obtained by the following proportion—

$$100 : 392.28 :: 1102.6 : 4323.7$$

=sp. gr. of phosphorus vapour.

Secondly, to find the specific gravity of a vapour like that of fluorine, of which the combining measure may be presumed to be two, or double that of oxygen. The atomic weight of fluorine being 233.8,

$$100 : 233.8 :: 1102.6 : 2584 =$$

twice the specific gravity of fluorine, being the weight of two volumes, and the specific gravity required is 1292.

These cases are examples of a general rule, that the specific gravity of a body in the state of vapour is obtained by multiplying the atomic weight of the body by 1102.6, the specific gravity of oxygen, and dividing by 100. The number thus found must then be divided by the number of volumes which are known to compose the combining measure of the vapour.

The specific gravities thus calculated are generally more accurate than those obtained by direct experiment, from the circumstance that the operation of taking the specific gravity of a gas is generally less susceptible of precision, than the chemical analyses on which the atomic weights are founded.

The densities of vapours, taken a few degrees above their condensing points, are generally a little greater than the truth, owing to a peculiarity in their physical constitution which was formerly explained (page 68). Of such bodies, therefore, the theoretical is a necessary check upon the experimental density. Indeed, the calculated should in all cases be considered and used as the true density.

RELATION BETWEEN THE CRYSTALLINE FORM AND ATOMIC
CONSTITUTION OF BODIES—DOCTRINE OF ISOMORPHISM.

Bodies on passing from the gaseous or liquid to the solid state, generally present themselves in crystals, or regular geometrical figures, which are the larger and more distinct, the more slowly and gradually they are produced. Their formation is readily observed in the spontaneous evaporation of a solution of sea-salt, or in the slow cooling of a hot and saturated solution of alum, which salts assume the forms of the cube and regular octohedron. The crystalline form of a body is constant, or subject only to certain geometrical modifications which can be calculated, and is most serviceable as a physical character for distinguishing salts and minerals. Between bodies of similar atomic constitution, a relation in form has been observed of great interest and beauty, which now forms a fundamental doctrine of physical science, like the subjects of atomic weights and volumes just considered.

Gay-Lussac first made the remark that a crystal of potash-alum transferred to a solution of ammonia-alum, continued to increase without its form being modified, and might thus be covered with alternate layers of the two alums, preserving its regularity and proper crystalline figure. M. Beudant afterwards observed that other bodies, such as the sulphates of iron and copper, might present themselves in crystals of the same form and angles, although the form was not a simple one like that of alum. But M. Mitscherlich first recognised this correspondence in a sufficient number of cases, to prove that it was a general consequence of similarity of composition in different bodies. To the relation in form, he applied the term *isomorphism* (from *ισος*, equal, and *μορφή*, shape), and distinguished bodies which assume the same figure as *isomorphous*, or (in the same sense) as *similiform* bodies. The law

at which he arrived is as follows :—The same number of atoms combined in the same way produce the same crystalline form ; and crystalline form is independent of the chemical nature of the atoms, and determined only by their number and relative position.

This law has not been established in all its generality, but perhaps no fact is certainly known which is inconsistent with it, while an indisposition which certain classes of elements have to form compounds at all similar in composition to those formed by other classes, limits the cases for comparison, and makes it impossible to trace the law, throughout the whole range of the elements, in the present state of our knowledge respecting them.

The relation of isomorphism is most frequently observed between salts, from their superior aptitude to form good crystals. Thus the arseniate and phosphate of soda are obtained in the same form, and are exactly alike in composition, each salt containing one proportion of acid, two of soda and one of water as bases, together with twenty-four atoms of water of crystallization. With a different proportion of water of crystallization, namely, with fourteen atoms, and the other constituents unchanged, the crystalline form is totally different, but is again the same in both salts. For every arseniate, there is a phosphate corresponding in composition and identical in form ; the isomorphism of these two classes of salts, is indeed perfect. The arsenic and phosphoric acids, contain each five proportions of oxygen to one of arsenic and phosphorus respectively, and are supposed to be themselves isomorphous, although the fact cannot be demonstrated, as the acids do not crystallize. The elements, phosphorus and arsenic, are also presumed to be isomorphous ; and the isomorphism of their acids and salts is referred to the isomorphism of the elements themselves ; isomorphous compounds in general appearing to arise from isomorphous elements uniting in the same manner with the same substance. The isomorphism of the sulphate, seleniate, chromate and manganate of the same base is likewise always clear and easily observed ; each of the acids in these cases containing three proportions of oxygen to one of selenium, sulphur, chromium and manganese, themselves presumed to be isomorphous. Of bases, the isomorphism of the class consisting of magnesia, oxide of zinc, oxide of cadmium

and the protoxides of nickel, iron and cobalt, is well marked in the salts which they form with a common acid, and is particularly observable in the double salts of these oxides, such as the sulphate of magnesia and potash, sulphate of zinc and potash, sulphate of copper and potash, which have all six atoms of water and a common form. The sulphates themselves of these bases differ, most of them affecting seven atoms of water of crystallization, while the sulphate of copper affects five; but those with the seven may likewise be crystallized in favourable circumstances with five atoms of water, and then all assume the form of the copper salt, thus exhibiting a second isomorphism like the arseniate and phosphate of soda.

The peroxides of the same class of metals with alumina and the oxide of chromium, which consist of two atoms of metal and three of oxygen, also afford an instructive example of isomorphism, particularly in their double salts. The sulphate of the peroxide of iron with sulphate of potash and twenty-four atoms of water, forms a double salt having the octohedral form of sulphate of alumina and potash or common alum, the same astringent taste, with other physical and chemical properties so similar, that the two salts can with difficulty be distinguished from each other. The salt is called iron-alum, and there are corresponding manganese and chrome alums, neither of which contains alumina, but the deutoxide of manganese and oxide of chromium in its place, with the proportions of acid and water, which exist in common alum. In all these salts another substitution may occur without change of form; namely that of soda or oxide of ammonium for the potash in the sulphate of potash, giving rise to the formation of what are called soda-alum and ammonia alum.

Certain facts have been supposed to militate against the principles of isomorphism, which require consideration.

1°. It appears that the corresponding angles of crystals reputed isomorphous are not always exactly equal, but are sometimes found to differ one or two degrees, although the errors of observation in good crystals rarely exceed 10' or 20' of a degree. But it has been shown by Mitscherlich that a difference may exist between the inclinations of two series of similar faces in different specimens of the same salt, of 59'; while it is also known that the angles of a crystal alter sensibly in their relative dimensions with a change of temperature (page 3).

The angles of crystals are, therefore, affected in their values within small limits by causes of an accidental character, and absolute identity in crystalline form may require the concurrence of circumstances which are not found together in the ordinary modes of producing many crystals, which are still truly isomorphous.

2°. It appears that the same body may assume in different circumstances, two forms which are totally dissimilar and have no relation to each other. Thus sulphur on crystallizing from solution in the bisulphuret of carbon or in oil of turpentine, at a temperature under 100°, forms octohedrons with rhombic bases, but when melted by itself and allowed to cool slowly, it assumes the form of an oblique rhombic prism on solidifying at 232°. These are incompatible crystalline forms, as they cannot be derived from one common form. Carbon occurs in the diamond in regular octohedrons, and in graphite or plumbago in six-sided plates, forms which are likewise incompatible. Sulphur and charcoal have each, therefore, two crystalline forms, and are said to be *dimorphous*, (from $\delta\iota\varsigma$, twice, and $\mu\omicron\rho\phi\eta$, shape). Carbonate of lime is another familiar instance of dimorphism, forming two mineral species, calc-spar and arragonite, which are identical in composition, but differ entirely in crystalline form. G. Rose has lately shewn that the first or second of these forms may be given to the granular carbonate of lime formed artificially, according as it is precipitated at the temperature of the air, or near the boiling point of water. Of its two forms, carbonate of lime most frequently affects that of calc-spar; but carbonate of lead which assumes the same two forms, and is therefore doubly isomorphous with carbonate of lime, chiefly affects that of arragonite, and is very rarely found in the other form. Had these carbonates, therefore, been each known only in its common form, their isomorphism would not have been suspected, an important observation, as the want of isomorphism between certain other bodies may be caused by their being really dimorphous, although the two forms have not yet been perceived. There is no physical impossibility in a body's assuming three different forms, or being *tri-morphous* as well as dimorphous, but no case of trimorphism has been hitherto observed.

3°. The observation of the isomorphism of bodies is of the greatest value as an indication that they possess a similar con-

stitution, and contain a like number of atoms of their constituents. But it must be admitted that the most perfect coincidence in form, or true isomorphism is likewise observed between certain bodies which are quite different in composition. Thus bisulphate of potash is dimorphous, and crystallizes in one of the two forms of sulphur (Mitscherlich). Nitrate of potash in common nitre has the form of arragonite, and occurs also, there is reason to believe, in microscopic crystals in the form of calc-spar. Nitrate of soda, again, has the form of calc-spar. Hypermanganate of barytes and the anhydrous sulphate of soda likewise crystallize in one form. Between the first pair, sulphur and bisulphate of potash, the absence of all analogy in composition is sufficiently obvious, notwithstanding their isomorphism. Between nitrate of potash and carbonate of lime, and between hypermanganate of barytes and sulphate of soda, there is no similarity of composition, on the ordinary view which is taken of the constitution of these salts, but both of these pairs have been assimilated, in speculative views of their constitution proposed by Mr. Johnston* in regard to the first pair, and by Dr. Clark† in regard to the second, which merit consideration, although the hypotheses cannot possibly be both correct, as they are based upon incompatible data. Besides these examples of identity of crystalline form without any well established relation in composition, many others might be quoted, if occurrence in the simple forms of the cube and regular octohedron should be allowed to constitute isomorphism. For example: carbon, sea-salt, arsenious acid and alum, all occur in octohedrons, although they are no way related in composition. But these simple forms are so common, that they can be held as affording no proof of isomorphism, unless in cases where it is to be expected from admitted similarity of composition, as between the different alums, or between chrome iron and octohedral iron ore.

But notwithstanding the occurrence of such apparently fortuitous coincidences in form, isomorphism must still be considered as the surest criterion of similarity of composition which we possess. Truly isomorphous bodies generally correspond in a variety of other properties besides external form. Arsenic and phosphorus resemble each other remarkably in

* Philosophical Magazine, third series, vol. 12, page 480.

† Records of General Science, vol. iv, page 45.

odour, although the one is a metal and the other a non-metallic body, while the corresponding arseniates and phosphates agree in taste, in solubility, in the degree of force with which they retain water of crystallization, and in various other properties. The seleniate and sulphate of soda, which are isomorphous, are both efflorescent salts, and correspond in solubility, even so far as to agree in an unwonted deviation from the usually observed increasing rate of solubility at high temperatures, both salts being more soluble in water at 100° than at 212°. In fact, isomorphism appears to be always accompanied by many common properties, and to be the feature which indicates the closest relationship between bodies.

It will afterwards appear that the more nearly bodies agree in composition, they are the more likely to act as solvents of each other, or to be miscible in the liquid form. An attraction for each other of the same character is probably the cause of the easy blending together of the particles of isomorphous bodies, and of the difficulty of separating them after they are once dissolved in a common menstruum; such isomorphous salts as the hypermanganate and hyperchlorate of potash, may, indeed, crystallize apart from the same solution, owing to a considerable difference of solubility; and potash-alum may be purified, in a great measure, by crystallization, from iron-alum, which is more soluble and remains in the mother-liquor; but most isomorphous salts, such as the sulphates of iron and copper, when once dissolved together, do not crystallize apart, but compose homogeneous crystals, which are mixtures of the two salts in indefinite proportions. This intermixture of isomorphous compounds is of frequent occurrence in minerals, and was quite inexplicable and appeared to militate against the doctrine of combination in definite proportions, till the power of isomorphous bodies to replace each other in compounds was recognized as a law of nature. Thus in garnet, which is a sili-

cate of alumina and lime ($\text{Al}^{\cdot\cdot}\text{Al}^{\cdot\cdot}\text{Si}_3 + 3\text{Ca}^{\cdot\cdot}\text{Si}_3$) the alumina is found often wholly or in part replaced by an equivalent quantity of peroxide of iron; while the lime at the same time may be exchanged for protoxide of iron or for magnesia, without the proper crystalline character of the mineral being destroyed.

The extent to which the isomorphous relations of bodies have been traced, will appear on reviewing the groups or na-

tural families in which the elements may be arranged, and observing the links by which the different groups themselves are connected; these classes not being abruptly separated, but shading into each other in their characters, like the classes created by the naturalist for the objects of the organic world.

CLASSIFICATION OF ELEMENTS.

The First class comprises four elementary bodies: oxygen, sulphur, selenium, tellurium. The three last of these elements exhibit the closest parallelism in their own properties, in the range of their affinities for other bodies, and in the properties of their analogous compounds. They all form gases with one atom of hydrogen, and powerful acids with three atoms of oxygen, of which the salts, the sulphates, seleniates and tellurates are isomorphous; and the same relation undoubtedly holds in all the corresponding compounds of these elements.

Oxygen has not yet been connected with this group by a certain isomorphism of any of its compounds, but a close correspondence between it and sulphur appears, in their compounds with one class of metals being alkaline bases of similar properties, forming the two great classes of oxygen and sulphur bases, such as oxide of potassium and sulphuret of potassium; and in their compounds with another class of elements being similar acids, giving rise to the great classes of oxygen and sulphur acids, such as arsenious and sulfarsenious acids. They farther agree in the analogy of their compounds with hydrogen, particularly of peroxide of hydrogen and persulphuret of hydrogen, both of which bleach and are remarkable for their instability; and in the analogy of alcohol and mercaptan, which last may be considered as an alcohol with its oxygen replaced by sulphur. This class is connected with the next by manganese, of which manganic acid is isomorphous with sulphuric acid, and consequently manganese with sulphur.

Second Class.—This class comprises magnesium, calcium, manganese, iron, cobalt, nickel, zinc, cadmium, copper, hydrogen, bismuth, chromium, aluminum, glucinum, vanadium, zirconium, yttrium, thorium. The protoxides of this class, including water, form analogous salts with acids. A hydrated acid, such as crystallized oxalic acid or the oxalate of water, corresponding with the oxalate of magnesia; hydrated sulphu-

ric acid (HO , $\text{SO}_3 + \text{HO}$) with the sulphate of magnesia (MgO , $\text{SO}_3 + \text{HO}$). The isomorphism of the salts of magnesia, zinc, cadmium and the protoxides of manganese, iron, nickel and cobalt is perfect. But water has not been shewn to be isomorphous with these oxides, although it greatly resembles oxide of copper in its chemical relations. Lime is not so closely related as the other protoxides of this group, being allied to the following class. But its carbonate, both anhydrous and hydrated, its nitrate and the chloride of calcium assimilate with the corresponding compounds of the group; while to its sulphate or gypsum, CaO , $\text{SO}_3 + 2\text{HO}$, one parallel and isomorphous compound, at least, can be adduced, a sulphate of iron, FeO , $\text{SO}_3 + 2\text{HO}$ (Mitscherlich), which is also sparingly soluble in water like gypsum.

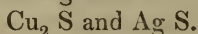
Bismuth is placed in this class from its nitrate and sub-nitrate, which are strictly analogous in composition to the nitrate and sub-nitrate of copper, but their isomorphism has not been observed. The salts of the oxide of chromium, of alumina and glucina are isomorphous with those of peroxide of iron (Fe_2O_3), with which these oxides correspond; and the salts of manganic and chromic acids are isomorphous, and agree with the sulphates. The vanadiates are believed to be isomorphous with the chromates. Zirconium is placed in this class, because its fluoride is isomorphous with that of aluminum and that of iron, and its oxide appears to have the same constitution as alumina; and yttrium and thorium solely because their oxides, supposed to be protoxides, are classed among the earths.

Third Class.—Barium, strontium, lead. The salts of their protoxides, barytes, strontian and oxide of lead are strictly isomorphous, and one of them, at least, oxide of lead is dimorphous, and assumes the form of lime, and the preceding class in the mineral plumbocalcite (Johnston). But certain carbonates of the second class are dimorphous, and enter into the present class, as the carbonate of lime in arragonite, carbonate of iron in junckerite, and carbonate of magnesia procured by evaporating its solution in carbonic acid water to dryness by the water-bath (G. Rose), which have all the common form of carbonate of strontian. Indeed these two classes are very closely related.

The Fourth class consists of potassium, ammonium, sodium,

silver. The term ammonium is applied to a hypothetical compound of one atom of nitrogen and four of hydrogen (NH_4), which is, therefore, certainly not an elementary body, and probably not even a metal, but which is conveniently assimilated in name to potassium, as these two bodies occupy the same place in the two great classes of potash and ammonia salts, between which there is the most complete isomorphism. Potassium and ammonium themselves are, therefore, isomorphous. The sulphates of soda and silver are similiform, and hence also the metals sodium and silver; but their isomorphism with the preceding pair is not so clearly established. Soda replaces potash in soda-alum, but the form of the crystal is the common regular octohedron; nitrate of potash has also been observed in microscopic crystals having the arragonitic form of nitrate of soda,* which is better evidence of isomorphism, although not beyond cavil as the crystals were not measured. There are also grounds for believing that potash replaces soda in equivalent quantities in the mineral chabasie, without change of form. The probable conclusion is that potash and soda are isomorphous, but that this relation is concealed by dimorphism, except in a very few of their salts.

This class is connected in an interesting way with the the other classes through the second. The sub-sulphuret of copper and the sulphuret of silver appear to be isomorphous, although two atoms of copper are combined in the one sulphuret and one atom of silver in the other, with one atom of sulphur; their formulæ being—



Are then *two* atoms of copper isomorphous with *one* atom of silver? In the present state of our knowledge of isomorphism, it will be wise to admit that they are.

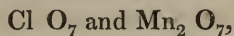
The fourth class will thus stand apart from the second which is represented by copper, and also from the other classes connected with the second, in so far as one atom of the present class is equivalent to two atoms of the other classes in the production of the same crystalline form. This discrepancy may be at once removed by halving the atomic weight of silver, and thus making both sulphurets to contain two atoms of me-

* Frankenheim in Poggendorff's *Annalen*, vol. 40, page 447. See also a paper by Professor Johnston on the received equivalents of potash, soda and silver; *Phil. Mag.* third series, vol. 12, p. 324.

tal to one of sulphur (Johnston *ubi supra*). But the division of the equivalents of sodium, potassium and ammonium which would follow that of silver, and the consideration of potash and soda as suboxides are most violent assumptions, and not to be lightly entertained.

It has been inferred that lime with an atom of water is probably isomorphous with potash and soda, because $\text{CaO} + \text{HO}$ appears to replace KO or NaO in mesotype, chabasie and other minerals of the zeolite family.

Fifth Class.—Chlorine, iodine, bromine, fluorine. These four elements form a well defined natural family. The three first are isomorphous throughout their whole combinations, chlorides with iodides, chlorates with iodates, hyperchlorates with hyperiodates, &c.; and such fluorides also as can be compared with chlorides appear to affect the same forms. It is connected with the second class through hyperchloric acid; the hyperchlorates being strictly isomorphous with the hypermanganates. But the formulæ of these two acids are—



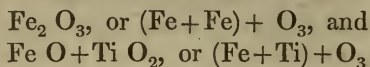
one atom of chlorine replacing two atoms of manganese. Or, this class has the same isomorphous relation as the preceding class to the others. And such I shall assume to be its true relation, although halving the atomic weight of chlorine, which would give two atoms of chlorine to hyperchloric acid, is not so improbable a supposition as dividing that of sodium; still it would lead to the strange conclusion that chlorine enters into its other compounds, as well as into hypermanganic acid, always in the proportion of two atoms; for that element is never known to combine in a less proportion than is expressed by its presently received equivalent. It appears that a salt has been casually observed to occur in the preparation of hypermanganate of potash having exactly the figure of chlorate potash, and containing a corresponding acid of manganese in which two of metal still represent one of chlorine as in hypermanganic acid.*

Sixth class. — Nitrogen, phosphorus, arsenic, antimony; also composing a well marked natural group, of which nitrogen and antimony are the two extremes, and of which the analogous

* Liebig's Introduction to the First Elements of Chemistry, by Richardson, page 87.

compounds exhibit isomorphism. These four elements all form gaseous compounds with three atoms of hydrogen, namely ammonia, phosphuretted, arsenuretted and antimonuretted hydrogen. The hydriodates of ammonia and of phosphuretted hydrogen are also isomorphous; so are arsenious acid and the oxide of antimony, both of which contain three atoms of oxygen to one of metal. Arsenious acid also is capable of replacing oxide of antimony in tartrate of antimony and potash or tartar emetic, without change of form, and arsenic often substitutes antimony in its native sulphuret. The nitrous acid (NO_3) which corresponds with arsenious acid and oxide of antimony, likewise acts occasionally as a base, as in the crystalline compound with sulphuric acid of the leaden chambers used in the manufacture of the latter acid. The complete isomorphism of the arseniates and phosphates has already been noticed. But phosphoric acid forms two other classes of salts, the pyrophosphates and metaphosphates, to which arsenic acid supplies no parallels. At present this class of elements can be connected by means of an isomorphous link with no other. It approaches most nearly to the fifth class, nitrogen and chlorine both forming a powerful acid with five proportions of oxygen, nitric acid and chloric acid; but of the many nitrates and chlorates which can be compared, no two have proved isomorphous. Nor do the metaphosphates appear at all like the nitrates, although their formulæ correspond.

Seventh class.—Tin, titanium. Connected by the isomorphism of titanous acid and peroxide of tin (Ti O_2 and Sn O_2). Titanium is connected in a curious manner with iron and the second class. Titanous acid occurs in ilmenite and other varieties of titanous iron, in combination with protoxide of iron, and in the crystalline form of the peroxide of that metal; namely, that of specular iron, and also of corundum (alumina). Hence,



are isomorphous. Now it is to be remarked that peroxide of iron and titanate of iron, although they agree in the number of their elements, each containing three of oxygen and two of metal, are yet not certainly analogous in proximate composition. If an acid of iron, consisting, like titanous acid, of one of metal and two of oxygen were known, which might be called

ferric acid, then specular iron would be a ferrate of the protoxide of iron, as the other is a titanate of the same base, and their isomorphism would be intelligible, and present nothing unusual. But if ferric acid does not exist, and it has hitherto eluded research, then the isomorphism of the bodies in question seems to imply that this relation does not require similarity of constitution, but merely equality in the number of atoms contained in the bodies which exhibit it.

Eighth Class.—Silver and gold. From their isomorphism in the metallic state. Gold will thus be connected, through silver, with sodium and the fourth class.

Ninth Class.—Platinum, palladium, iridium, osmium. From the isomorphism of their double chlorides. The bichloride of tin with chloride of potassium crystallizes in regular octohedrons, like the double bichloride of platinum and potassium, and other double chlorides of this group; which although not alone sufficient to establish an isomorphous relation between this class and the seventh, yet favours the notion of its existence (Dr. Clark.)

Tenth class.—Tungsten and molybdenum. From the isomorphism of the tungstates and molybdates, the salts of tungstic and molybdic acids, $W O_3$ and $Mo O_3$. Mr. Johnston has observed that the chromate of lead is dimorphous, and corresponds in the least usual of its forms with the molybdate of lead. This establishes a relation between molybdic, chromic, sulphuric and other analogous acids.*

Eleventh Class.—Carbon, boron, silicon. These elements are placed together from a general resemblance which they exhibit without any precise relation. They are not known to be isomorphous among themselves, or with any other element. They are non-metallic, and form weak acids with oxygen,—the carbonic, consisting of two of oxygen and one of carbon, and the boracic and silicic acids, which are generally viewed as composed of three of oxygen to one of boron and silicon. Silicic acid may, perhaps, replace alumina in some minerals, but this is uncertain.

Of the elements which have not been classed, no isomorphous relations are known. They are mercury, which in some of its chemical properties is analogous to silver, and in others

* Phil. Mag. third series, vol. 12, p. 387.

to copper, cerium, columbium, lithium, rhodium and uranium.

According to the original law of Mitscherlich, that isomorphism depends upon equality in the number of atoms, and similarity in their arrangement, without reference to their nature, the elements themselves should all be isomorphous. Most of the metals crystallize in the simple forms of the cube or regular octohedron, which are not sufficient to establish this relation. But the isomorphism of a large proportion, if not the whole, of the elements may be inferred from the isomorphism of their analogous compounds. Thus from the facts just adduced, it appears that the members of the following large class of elements are linked together from the isomorphism of one or more of their compounds. This large class may be subdivided into smaller classes, between the members of which, isomorphism is of more frequent occurrence, and which are then to be viewed as isomorphous groups.

ISOMORPHOUS ELEMENTS.

1. Sulphur
Selenium
Tellurium

2. Magnesium
Calcium
Manganese
Iron
Cobalt
Nickel
Zinc
Cadmium
Copper
Chromium
Aluminum
Glucinum
Vanadium
Zirconium

3. Barium
Strontium
Lead

4. Tin
Titanium

5. Tungsten
Molybdenum.

With two atoms of the preceding elements.

6. Sodium
Silver
Gold
Potassium
Ammonium

7. Chlorine
Iodine
Bromine
Fluorine

The only known group of isomorphous elements which cannot

be connected in a probable manner with the above large class, is that of

Nitrogen

Arsenic

Phosphorus

Antimony

The tendency of discovery is to bring all the elements into one class, either as isomorphous atom to atom, or with the relation to the others which chlorine and sodium exhibit.

But must not isomorphism be implicitly relied upon in estimating atomic weights, and the alterations which it suggests be adopted without hesitation in every case? Chemists have always been most anxious to possess a simple physical character by which atoms might be recognised; and equality of volume in the gaseous state, equality of specific heat, and similarity in crystalline form have all in their turn been upheld as affording a certain criterion. The indications of isomorphism certainly accord much better than those of the other two criteria with views of the constitution of bodies derived from considerations purely chemical, and are indeed invaluable in establishing analogy of composition in a class of bodies, by supplying a precise character which can be expressed in numbers, instead of that general and ill-defined resemblance between allied bodies, which chemists perceived by an acquired tact rather than by any rule, and which was heretofore their only guide in classification. Admitting that isomorphism is a certain proof of similarity of atomic constitution within a class of elements and their compounds, it may still be doubted whether the relation of the atom to crystalline form is the same without modification throughout the whole series of the elements, or whether all atoms agree exactly in this or any other physical character.

Crystalline form and the isomorphous relation may prove not to be a reflection of atomic constitution, or immediately and necessarily connected with it, but to arise from some secondary property of bodies, such as their relation to heat; in which a simple atom may occasionally resemble a compound body, as we find sulphur isomorphous in one of its forms, with bisulphate of potash. While we find another simple atom, potassium, isomorphous through a long series of compounds with the group of five atoms which constitute ammonium. The occurrence of dimorphism also both in simple and compound bodies gives to crystalline form a secondary character.

Is it probable that sulphur and carbonate of lime could be made to appear in sets of crystals which are wholly unlike, merely by a slight change of temperature, if form were the consequence of an invariable atomic constitution? Crystalline form then may possibly depend upon some at present unknown property of bodies, which may have a frequent and general, but certainly not an invariable relation to their atomic constitution. There may be nothing truly inconsistent with the principles of isomorphism in one atom of a certain class of elements having the same crystallographic value as two atoms of another class, the relation which has been assumed to exist between the sodium and chlorine classes and the others, particularly when the classes stand apart, and differ in their properties from all the others, as those of sodium and chlorine do.

The atomic weight of hydrogen ought not to be divided or reduced from 12.5 to 6.25, for that element certainly belongs to the natural family of magnesium or the second class, of which the equivalents must remain fixed, as they are practically the standards of comparison for all others. If hydrogen be divided, so must magnesium, calcium, manganese and the whole class. But it has at last been admitted that hydrogen never combines in a less proportion than 12.5, and the indivisibility of its equivalent therefore conceded;* although it is proposed to make a distinction between the values of the equivalent and of the atom of a body which is altogether uncalled for.

DIMORPHISM.

Many solid bodies admit of a variation of properties while in that state of which gases and liquids are not susceptible. The assumption of two incompatible crystalline forms by the same body, in different circumstances, has already been noticed as occurring with sulphur, carbon, carbonates of lime and lead, bisulphate of potash and chromate of lead. It is also observed, in the biphosphate of soda, and in a considerable number of minerals. The dimorphous crystals may differ in density, the densities of calc-spar and arragonite, the forms of carbonate of lime, being 2.719 and 2.949, and indeed all resemblance in properties between the crystals may be lost, as in

* By Berzelius. L'Institut, May 1838, page 160.

diamond and graphite, the two forms of carbon. The particular form assumed by sulphur and carbonate of lime, which may be made to crystallize in either of their forms at will, is found to depend upon the degree of temperature at which the solid is produced; carbonate of lime being precipitated, on adding chloride of calcium to carbonate of ammonia, in a powder, of which the grains have the form of calc-spar or of arragonite, according as the temperature of the solution is 50° or 150° .* A large crystal of arragonite when heated by a spirit-lamp, decrepitates and falls into a powder composed of grains of calc-spar. The crystals of sulphur produced at the higher of two temperatures, become opaque when kept for some days in the air, and pass spontaneously into the other form; while the crystals produced at the lower temperature are disintegrated, and changed into the other form by a moderate heat. These observations are important as establishing a relation between dimorphism and solidification at different temperatures.

A considerable variation of properties is likewise often observable in a solid, which is not crystalline, or of which the crystalline form is indeterminate. Thus sulphuret of mercury obtained by precipitating corrosive sublimate by sulphureted hydrogen, is black; but the same body when sublimed by heat, or produced by agitating mercury in a solution of the persulphuret of potassium, forms cinnabar, of which the powder is the red pigment vermilion; while vermilion itself, if heated till sulphur begins to sublime from it, and then suddenly thrown into cold water, becomes black; although if allowed to cool slowly it remains red. Yet it is of the same composition exactly in the black and red states. The iodide of mercury newly sublimed is of a lively yellow colour, and may remain so for a long time, but it generally begins to pass into a fine scarlet on cooling, and may be made to undergo this change of colour, in an instant, by strongly pressing it. The precipitated sulphuret of antimony may be deprived of the water it contains, at the melting point of tin, without losing its peculiar orange colour; but when heated a little above that temperature, it shrinks and assumes the black colour and metallic lustre of the native sulphuret, without any loss of weight. Again the black sulphuret when heated strongly and thrown into water, loses

* G. Rose, Phil. Mag. 3d Series, vol. 12, p. 465.

its metallic lustre, and acquires a good deal of the appearance of the precipitated sulphuret. The nitrites are sometimes white and sometimes yellow ; and crystals of sulphate of manganese are often deposited from the same solution, some of which are pink and others colourless, although identical in composition.

Such differences of colour are permanent, and not to be confounded with changes which are peculiar to certain temperatures: thus oxide of zinc is of a lemon yellow colour, when strongly heated, but milk-white at a low temperature; the oxide of mercury is much redder, at a high than at a low temperature, and bichromate of potash, which is naturally red, becomes almost black when fused by heat. Even bodies in the gaseous state are liable to transient changes of this kind, the brown nitrous fumes being nearly colourless below zero, and on the other hand deepening greatly in colour at a high temperature.

The condition of *glass* is a remarkable modification of the solid form assumed by many bodies. Matter in this state is not crystallized, and on breaking presents curved and not plain surfaces, or its fracture in mineralogical language is *conchoidal*, and not *sparry*. The indisposition to crystallize, which causes solidification in the form of glass, is more remarkable in some bodies, such as phosphoric and boracic acids, and their compounds, than in others. The biphosphate and binarsenate of soda have the closest resemblance in properties, yet when both are fused by a lamp, the first solidifies on cooling into a transparent colourless glass, and the second into a white opaque mass composed of interlaced crystalline fibres. The phosphate at the same time discharges sensibly less heat, than the arseniate in solidifying, retaining probably a portion of its heat of fluidity or latent heat in a state of combination, while a glass. None of the compounds of silicic acid and a single base, or simple silicates, becomes a glass on cooling from a state of fusion, with the exception of the silicate of lead containing a great excess of oxide: they all crystallize. But a *mixture* of the same silicates when fused, exhibits a peculiar viscosity or tenacity, appears to have lost the faculty of crystallizing, and constantly forms a glass. The varieties of glass in common use are all such mixtures of silicates. Glass is sometimes devitrified when kept soft by heat for a long time, owing to the separation

of the silicates from each other and their crystallization; and the less mixed glasses are known to be most liable to this change. It is probable that all bodies differ when in the vitreous and in the crystalline forms in the proportion of combined heat which they possess, as has been observed of melted sugar (page 43) in these two conditions.

Arsenious acid when fused or newly sublimed appears as a transparent glass of a light yellow tint. But left to itself, it slowly becomes opaque and milk white; the change commencing at the surface and advancing to the centre, and often requiring years to complete it in a considerable mass. The arsenious acid is no longer vitreous, being changed into a multitude of little crystals, whence results its opacity; and it has altered slightly at the same time in density and in solubility. But the passage from the vitreous to the crystalline state may take place instantaneously, and give rise to an interesting phenomenon lately observed by H. Rose. The vitreous arsenious acid seems to dissolve in dilute and boiling hydrochloric acid without change, but the solution on cooling deposits crystals which are of the opaque acid, and a flash of light, which may be perceived in the dark, is emitted in the formation of each crystal. This phenomenon depends upon and indicates the transition, for it does not occur when arsenious acid already opaque is substituted for vitreous acid, and dissolved and allowed to crystallize in the same manner.

A still greater change than those described, is induced upon certain bodies by exposure to a high temperature, without any corresponding change in their composition. Several metallic peroxides, such as alumina, oxide of chromium and peroxide of tin cease to be soluble in acids after being heated to redness. The same is true of a variety of salts, such as many phosphates, antimonates and silicates. All these bodies contain water in combination, when most readily dissolved by acids, which constituent is dissipated at a high temperature, but in general before the loss of solubility occurs, so that the contained water alone is not the cause of the solubility. Berzelius remarked an appearance often observable when such bodies are under the influence of heat, and in the act of passing from the soluble to the insoluble state. They suddenly glow or become luminous, rising in temperature above the containing vessel, from a discharge of heat. The rare mineral gadolinite affords a

beautiful example of this change. When heated it appears to burn, emits light, and becomes yellow, but undergoes no change in weight. Many bodies exhibit a feeble phosphorescence when heated, which has no relation to this change and is to be distinguished from it.

The circumstance most certain respecting this change in bodies, which affects so deeply their chemical properties, is that the bodies do not contain a quantity of heat, after the change, which they must have possessed before its occurrence in a combined or latent form. No ponderable constituent is lost, but there is this loss of heat. A change of arrangement of the particles, it is true, might occur at the same time in some of these bodies, such as is observed when sulphite of soda is converted by heat into a mixture of sulphate of soda and sulphuret of sodium, without change of weight; but it would be difficult to apply an explanation of this nature to oxides, such as alumina and peroxide of tin, which contain only two constituents. The loss of heat observed will afford all the explanation necessary if heat be admitted as a constituent of bodies equally essential as their ponderable elements. As the oxide of chromium possesses more combined heat when in the soluble than in the insoluble state, the first may justly be viewed as the higher *caloruret*, and the body in question may have different proportions of this as well as of any other constituent. But it is to be regretted that our knowledge respecting heat as a constituent of bodies is extremely limited; the definite proportion in which it enters into ice and other solids in melting, and into steam and vapours has been studied, and also the proportion emitted during the combustion of many bodies, which has likewise proved to be definite. But the influence which its addition or subtraction may have on the chemical properties of a body is at present entirely matter of conjecture. The phenomena under consideration seem to require the admission of heat as a true constituent which can modify the properties of bodies very considerably, otherwise a great physical law must be abandoned, namely, that "no change of properties can occur without a change of composition." But if heat be once admitted as a chemical constituent of bodies, then a solution of the present difficulties may be looked for, for nothing is more certain than that "a change in composition will account for any change in properties." Heat thus combined in definite pro-

portions with bodies and viewed as a constituent, must not be confounded with the specific heat of the same bodies or their capacity for sensible heat, which may have no relation to their combined heat.

ISOMERISM.

In such changes of properties the individuality of the body is never lost. But numerous instances have presented themselves of two or more bodies possessing the same composition, which are unquestionably different substances and not mutually convertible into each other. Different bodies thus agreeing in composition but differing in properties are said to be *isomeric*, (from *ισος*, equal, and *μερος*, part), and their relation is termed *isomerism*. The discovery of such bodies excited much interest and they have received of late years a considerable share of the attention of chemists. But the result of a careful study of the bodies associated by similarity of form, though differing in properties, has been upon the whole unfavourable to the doctrine of isomerism. Isomeric bodies have in general been found to agree in the relative proportion of their constituents only, and to differ either in the aggregate number of the atoms composing them, or in the mode of arrangement of these atoms; and very few cases of isomerism now remain which do not admit of explanation. This is what was to be expected, for isomerism in the abstract is improbable, a difference in properties between bodies, without a difference in their composition, appearing to be an effect without a sufficient cause. Hence, the term isomerism is now generally employed in a limited sense, to indicate simply the identity in composition of two or more bodies as expressed in the proportion of their constituents in 100 parts. Several classes of such isomeric bodies may be formed.

The members of the most numerous class of isomeric bodies differ in atomic weight. Thus we know at present three gases, three or four liquids, and as many solids which all consist exactly of carbon and hydrogen in the proportion of one atom to one atom, or in weight, of 86 parts of carbon and 14 of hydrogen very nearly. These bodies agree in ultimate composition, but differ completely in every other respect. But a representation of their chemical constitution explains at once the cause of the diffe-

rences they present, as is obvious in the following formulæ of four of the best characterized members of this isomeric group :

				Equivalents and combining measure.	
Methylene.	.	.	.	$C_2 H_2$	or 4 volumes.
Olefiant gas.	.	.	.	$C_4 H_4$	or 4 volumes.
Gas from oil.	.	.	.	$C_8 H_8$	or 4 volumes.
Cetene.	.	.	.	$C_{32} H_{32}$	or 4 volumes.

It thus appears that the atom of cetene contains four times as many atoms of carbon and hydrogen as the atom of the gas from oil, eight times as many as the atom of olefiant gas, and sixteen times as many as the atom of methylene ; while as the atom of all these bodies affords the same measure of vapour or four volumes, they must differ as much in density as they do in the number of their constituent atoms. It is not surprizing, therefore, that they all possess different and peculiar properties. Several groups of bodies might be selected from Table II, at page 134, which have a similar relation to each other, the number of their atoms being different, although their relative proportion is the same, such as :

Oil of lemons.	.	.	.	$C_{10} H_8$
Oil of turpentine.	.	.	.	$C_{20} H_{16}$

and,

Naphthaline.	.	.	.	$C_{20} H_8$
Paranaphthaline.	.	.	.	$C_{30} H_{12}$

A still more remarkable case is presented to us in alcohol, and the ether from wood-spirit, in which there is identity of condensation as well as of composition, with different equivalents. Their vapours have in fact the same specific gravity, and contain under equal volumes, equal quantities of carbon, hydrogen and oxygen. But we know that each of these bodies is composed of two others, alcohol of one atom of olefiant gas, and two atoms of water ; and the ether of wood-spirit, of one atom of methylene, and one of water, so that their constitution and rational formulæ are quite different :

Alcohol.	.	.	.	$C_4 H_4 + 2HO$
Ether of wood spirit.	.	.	.	$C_2 H_2 + HO$

In another class of isomeric bodies, the atomic weight may be equal, as well as the elementary composition. A pair belonging to this class are known, which coincide besides in the specific gravity of their vapours. The composition and atom

of both formic ether and the acetate of methylene may be represented by $C_6 H_5 O_4$, the density of both their vapours is 2574 ; and what is very remarkable, these bodies in their ordinary liquid state almost coincide in properties, the density of formic ether being 0.916, and that of the acetate of methylene 0.919, (density of water being 1000), while the first boils at 133° , and the last at 136.4° . But when acted on by alkalies, their products are entirely different, the one affording formic acid and alcohol, and the other acetic acid and wood-spirit. Each of the isomeric bodies in question contains, indeed, two different binary compounds, and their constitution is truly represented by different formulæ :

Formic ether. $C_4 H_5 O + C_2 H O_3$

Acetate of methylene. $C_2 H_3 O + C_4 H_3 O_3$

in which the same atoms are seen to be very differently arranged.

The last class of isomeric bodies are of the same atomic weights, but their constitution or molecular arrangement being unknown, their isomerism, cannot at present be explained. It can scarcely be doubted, however, that their molecular arrangement is really different. Cyanic and fulminic acids are in this predicament, their common formula being $N C_2 O$. Malic and citric acids were also believed to present a similar relation, but recent discoveries respecting the constitution of their salts have separated these and several other acids heretofore viewed as isomeric.

One pair, however, of isomeric bodies remains which have defeated every attempt at explanation, the racemic and tartaric acids, which exhibit a similarity of properties, and a parallelism in their chemical characters that are truly astonishing. These acids are found together in the grape of the upper Rhine. They differ considerably in solubility, the racemic being the least soluble, so that they may be separated from each other by crystallization ; and the racemic acid contains an atom of water of crystallization, which is not found in the crystals of tartaric acid. They form salts which correspond very closely in their solubility and other properties. The bitartrate and biracemate of potash are both sparingly soluble salts: the tartrates and racemates of lime, lead and barytes are all alike insoluble. Both acids form a double salt with soda and ammonia, which is an unusual kind of combination. But what is most surprising,

crystals of these double salts, not only coincide in the proportion of their water and other constituents and in the composition of their acids but also in external form, having been observed by Mitscherlich to be isomorphous. A nearer approach to identity could scarcely be conceived than is exhibited by these bodies, which are, indeed, the same both in form and composition. The crystallized acids are both modified in an unusual manner by heat, and form three classes of salts, as phosphoric acid does. The formula of both acids in their ordinary class of salts is $C_8 H_4 O_{10}$ + two atoms of base (Fremy). But by no treatment can the one acid be transmuted into the other. Lastly, every organic acid produces a new acid by destructive distillation, which is peculiar to it and is termed its pyr-acid. Now racemic and tartaric acid, when destroyed by heat, agree in giving birth to one and the same pyr-acid.

ARRANGEMENT OF THE ELEMENTS IN COMPOUNDS.

The names of some compounds imply that they contain other compounds, and indicate a certain atomic constitution, while the names of other compounds express no particular arrangement of their constituent atoms, but leave it to be inferred that the atoms are all directly combined together. Thus sulphate of soda implies the continued existence of sulphuric acid and soda in the salt, while nitric acid or peroxide of hydrogen, supposes no partition of the compound to which it is applied. But it is to be remembered that the original framers of the nomenclature were guided more by facilities of an etymological nature in constructing such terms, than by views of the constitution of compounds.

Of a binary compound containing single atoms of its constituents, there cannot be two modes of representing the constitution, but where one of the constituents is present in the proportion of two or more atoms, several hypotheses can always be formed of their mode of aggregation. In a series of binary combinations of the same elements, such as that of nitrogen and oxygen, NO , NO_2 , NO_3 , NO_4 , NO_5 , the simplest view has generally been taken, namely that it is the elements themselves which unite. But in particular cases the chemist is often involuntarily led into another opinion. Thus deutoxide of nitrogen is so often a product of the decomposition of nitric acid,

that it appears more like a compound of that oxide of nitrogen with oxygen, than a compound of nitrogen itself with oxygen. When the peroxide of hydrogen was first discovered by Thénard, he was led by the whole train of its properties to view it as a compound of water and oxygen, into which it is resolved with so much facility, and to name it accordingly *oxygenated water*, which it may be, and not a direct combination of hydrogen and oxygen; or its formula may be $\text{HO} + \text{O}$, and not HO_2 . The periodide of potassium and the other analogous compounds obtained by dissolving iodine in metallic iodides, were first termed *ioduretted iodides* from similar considerations, and the hyposulphites, obtained by dissolving sulphur in sulphites, *sulphuretted sulphites*. It may be doubted whether chemists would return with advantage to any of these expressions, the views of composition which they indicate being uncertain, and not offering a sufficient inducement to depart from the more systematic designations. The peroxide of hydrogen, for instance, may be easily resolved into water and oxygen, not because water pre-exists in it, but because water is a compound of great stability and is formed when peroxide of hydrogen is decomposed. Nitric acid, also, is as likely to be a compound of peroxide of nitrogen with an additional atom of oxygen, as of deutoxide of nitrogen, with three atoms of the same element.

Certain compound bodies, however, have been observed to act the part of a simple body in combination, and can be traced through a series of compounds. The following substances, for instance, may be represented with considerable probability as compounds of carbonic oxide, as in the formulæ :

CO , carbonic oxide.

$\text{CO} + \text{O}$, carbonic acid.

$\text{CO} + \text{Cl}$, chloroxycarbonic acid.

$2\text{CO} + \text{O}$, oxalic acid.

$2\text{CO} + \text{Cl}$, chloroxalic acid.

Carbonic oxide is said to be the *radical* of this series, a name applied to any compound which is *capable of combining with simple bodies*, as carbonic oxide appears to do with oxygen and chlorine in these compounds. Messrs. Liebig and Wöhler have shewn by decisive experiments that such a radical exists in the benzoic combinations, which may be represented thus :

$\text{C}_{14} \text{H}_5 \text{O}_2 + \text{O}$, benzoic acid.

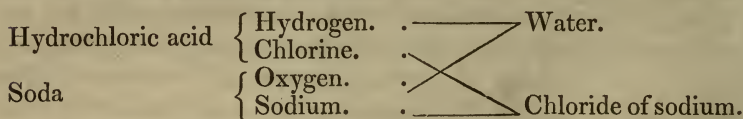
$\text{C}_{14} \text{H}_5 \text{O}_2 + \text{H}$, essential oil of almonds

$\text{C}_{14} \text{H}_5 \text{O}_2 + \text{Cl}$, chloride of benzoyle, etc.

Cyanogen was the first recognised member of the class of compound radicals, of which the number known to chemists is constantly increasing, and which appear to pervade the whole compounds of organic chemistry. In combining with simple bodies, radicals act the part of other simple bodies, such as metals, chlorine, oxygen, etc., which they replace in compounds.

Constitution of salts. Of the supposed combinations of binary compounds with binary compounds, the most numerous and important class are salts. Sulphate of soda is commonly viewed as a direct combination of sulphuric acid and soda, each preserving its proper nature in the compound; and so are all similar compounds of an acid oxide with a basic oxide. An oxygen acid is allowed to exist in them, and they are particularly distinguished as "oxygen-acid salts." But an opinion was promulgated long ago by Davy, that these salts might be constituted on the plan of the binary compounds of the former class, and their hydrated acids on the plan of a hydrogen acid; a view which is supported by many analogies, and has latterly had a preference given to it by some of our leading chemical authorities. It is, therefore, deserving of serious consideration.

One class of acids, the hydrogen acids, and the salts which they produce with alkalis, are unquestionably binary compounds, and were assumed by Davy as the types of acids and salts in general. Hydrochloric acid is composed of two elements, chlorine and hydrogen, and with soda it forms water and chloride of sodium, thus:



the hydrogen of the acid being replaced by sodium in the salt formed. Hydrocyanic is another hydrogen acid, of which cyanide of sodium is a salt. In general terms, a *radical* (which may be either simple or compound, like chlorine or cyanogen) forms an *acid* with hydrogen, and a *salt* with sodium or any other metal.

Hydrated sulphuric acid, which consists of sulphuric acid and an atom of water, $\text{HO} + \text{SO}_3$, is represented as a hydrogen acid by transferring the oxygen of the water to the sulphuric acid, to form a new radical, SO_4 , which is supposed to be in direct combination with the remaining atom of hydrogen, as $\text{H} + \text{SO}_4$. In sulphate of soda, the oxygen of the soda is in the same

manner transferred to the acid, or the formula of the salt is changed from $\text{NaO} + \text{SO}_3$ to $\text{Na} + \text{SO}_4$. To SO_4 , which is generally spoken of as the "sulphate radical," the name *sulphatoxygen* may be applied, and its compounds be called *sulphatoxides*; and then the acid and salt will be thus named and denoted on the two views of their constitution :

Old view :

Hydrated sulphuric acid or sulphate of oxide of hydrogen.	$\text{HO} + \text{SO}_3$
Sulphate of soda or sulphate of oxide of sodium.	$\text{NaO} + \text{SO}_3$

New view :

Sulphatoxide of hydrogen.	$\text{H} + \text{SO}_4$
Sulphatoxide of sodium.	$\text{Na} + \text{SO}_4$;

which last formulæ are strictly comparable with those of an admitted hydrogen acid and its salt, such as :

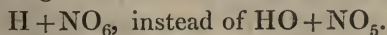
Hydrochloric acid or chloride of hydro- gen.	$\text{H} + \text{Cl}$
Chloride of sodium.	$\text{Na} + \text{Cl}$;

or as :

Hydrocyanic acid or cyanide of hydro- gen.	$\text{H} + \text{NC}_2$
Cyanide of sodium.	$\text{Na} + \text{NC}_2$;

which thus appear compounds of three different radicals, chlorine (Cl), cyanogen (NC_2), and sulphatoxygen (SO_4), with the same elementary bodies, hydrogen and sodium. Sulphatoxygen is known only in combination, and has not been obtained in a separate state like chlorine and cyanogen. The body, sulphuric acid, SO_3 , which may be separated from some sulphates and can exist by itself, is supposed to be a product of their decomposition and not to pre-exist in these salts, so that it has a secondary character assigned to it.

Hydrated nitric acid, or aqua fortis, becomes a hydrogen acid, by the creation of a nitrate radical, nitratoxygen. It is the nitratoxide of hydrogen instead of the nitrate of water,



The nitrate of potash becomes the nitratoxide of potassium, and so of all other nitrates. The existence of nitratoxygen is hypothetical, as it has not been insulated, but in this respect it is not otherwise situated than nitric acid itself, which cannot be

exhibited in a separate state, and is believed to be capable of existing only in a state of combination.

It is evident that the same view is applicable to hydrated oxygen acids in general, which may be made hydrogen acids, by assuming the existence of a new radical for each, containing an atom more of oxygen than the oxygen acid itself, and capable of combining directly with hydrogen and the metals. The class of oxygen-acid salts is thus abolished, and they become binary compounds like the chlorides and cyanides. Even oxygen-acids themselves can no longer be recognized. It is not sulphuric acid (SO_3), but what was formerly viewed as its compound with water, that is the acid, and it is a hydrogen acid. The properties which characterize acids are undoubtedly only observed in the hydrates of the oxygen acids. Thus the anhydrous sulphuric acid does not redden litmus, and exhibits a disposition to combine with salts, such as chloride of potassium and sulphate of potash, rather than with bases. The liquid carbonic acid has little affinity for water, does not combine directly with lime, but dissolves in alcohol, ether and essential oils like certain neutral bodies. It is only when associated with water that the bodies referred to exhibit acid properties, and then hydrogen acids may be produced.

On this view, it is obvious that the acid and salt are really bodies of the same constitution, hydrochloric acid being the chloride of hydrogen, as common salt is the chloride of sodium, and sulphuric acid and sulphate of soda, being the sulphatoxides of hydrogen and of sodium. The acid reaction and sour taste are not peculiar to the hydrogen compound and do not separate it from the others, the chloride, sulphatoxide and nitratoxide of copper being nearly as acid and corrosive as the chloride, sulphatoxide and nitratoxide of hydrogen, and clearly bodies of the same character and composition. They are all equally salts in constitution. The theory in question, therefore, is truly a theory of salts, and might be distinguished as "the theory of Binary Salts," or some such name, with more propriety than the theory of hydrogen-acids. The term "acid" is not absolutely required for any class of bodies included in the theory, and might, therefore, be dropt, if it were not that an inconvenience would be felt in having no common name for the hydrogen compounds, which have so many common uses. But overlooking this consideration, the supporters of

this theory might, perhaps, simplify the expression of it, and conciliate their opponents by allowing that class of bodies to retain the name of acid which first bore it, although, of course, in a sense consistent with their own views. It would then be such bodies as anhydrous sulphuric acid (SO_3), anhydrous nitric acid (NO_5), that would compose the class of "acids;" and in considering the generation of salts, three orders of bodies would be admitted, as in the following tabular exposition of a few examples :

I.	II.	III.
The acid.	The salt-radical.	The salt.
SO_3	SO_4	$\text{SO}_4 + \text{H}$ or a Metal.
NO_5	NO_6	$\text{NO}_6 + \text{H}$ or a Metal.
	NC_2	$\text{NC}_2 + \text{H}$ or a Metal.
	Cl	$\text{Cl} + \text{H}$ or a Metal.

The first term of the series, or "the acid," is wanting in the last two examples, and that is the peculiarity of those bodies which constituted the original class of hydrogen acids and their salts. While the old class of oxygen-acid salts have both a radical and an acid, as in the first two examples.

The peculiar advantages of the Binary Theory of Salts, are—

First: That instead of two it makes but one great class of salts, assimilating in constitution bodies which certainly resemble each other in properties. Chloride of sodium and sulphate of soda are both neutral, and possess a common character, which is that of a soda-salt, but they are separated widely from each other on the ordinary view of their constitution which is expressed in their names.

Secondly: It accounts for a remarkable law which is observed in the construction of salts; namely, that bases always combine with as many atoms of acid, as they themselves contain of oxygen; a protoxide, which contains one atom of oxygen combining and forming a neutral salt with one atom of an oxygen acid; while an oxide which contains two atoms of oxygen to one of metal, like peroxide of tin, forms a neutral salt with two atoms of acid; and an oxide of three atoms of oxygen to two of metal, like peroxide of iron, forms a neutral salt with three atoms of acid. The acid and oxygen are thus always together in the exact proportion to form the salt-radical, there being always an atom of oxygen for every atom of acid in the salt. This will appear more distinctly in the following

formulae which exhibit the composition of the neutral sulphates of a metal in four different states of oxidation, an atom of metal being represented by M.

Formulae of neutral sulphates.

I.	II.	As consisting of oxide and acid.		As consisting of metal and salt-radical.	
$\text{MO} + \text{SO}_3$.	$\text{M} + \text{SO}_4$.	as in sulphate of soda.	
$\text{M}_2\text{O} + \text{SO}_3$.	$\text{M}_2 + \text{SO}_4$.	as in sulphate of suboxide of mercury.	
$\text{MO}_2 + 2\text{SO}_3$.	$\text{M} + 2\text{SO}_4$.	as in sulphate of peroxide of tin.	
$\text{M}_2\text{O}_3 + 3\text{SO}_3$.	$\text{M}_2 + 3\text{SO}_4$.	as in sulphate of peroxide of iron.	

The acid is seen in the first column to be always in the proper proportion to form a sulphatoxide of the metal in the second column; and these sulphatoxides correspond exactly with known chlorides, such as M Cl , $\text{M}_2 \text{Cl}$, M Cl_2 , $\text{M}_2 \text{Cl}_3$.

Thirdly: It offers a more simple and philosophical explanation of the action of certain metals upon acid solutions, and of the decomposition of such solutions in other circumstances. Thus when zinc is introduced into hydrochloric acid, it is allowed on both views, that the metal simply displaces the hydrogen which is evolved, and that chloride of zinc is formed in the place of chloride of hydrogen. In the same way when zinc is introduced into diluted sulphuric acid, which contains the sulphatoxide of hydrogen on the binary theory, hydrogen is simply displaced and evolved as before, and the sulphatoxide of zinc formed instead of the sulphatoxide of hydrogen. The metal in question appears to be incapable of decomposing pure water by displacing its hydrogen at the temperature of the air; but this fact does not interfere with the preceding explanation, as zinc may have a greater affinity for sulphatoxygen than for oxygen, and, therefore, be capable of decomposing the sulphatoxide, but not the oxide of hydrogen. If the acid solution, however, contains sulphate of water, as it does on the old view, then zinc does and does not decompose water, decomposing it when in combination, but not when free. It then becomes necessary to assume that the presence of the acid enhances the affinity of the metal for the oxygen of the water, in a manner which cannot be clearly explained; for the solu-

bility of oxide of zinc in the acid, to which its influence is generally ascribed, accounts for the continuance of the action, by providing for the removal of the oxide, rather than for its first commencement. The phenomena of the decomposition of an acid solution by electricity, are also most simply explained on the binary theory. Oxide of hydrogen and sulphatoxide of hydrogen, are both binary 'electrolytes,' which are decomposed by the electric current in the same manner, although not with equal facility, the common element, hydrogen, proceeding from both to the negative electrode, and the oxygen in the one case and the sulphatoxygen in the other to the positive electrode. The sulphatoxygen finds water there, and resolves itself into sulphatoxide of hydrogen and free oxygen. The decomposition of the sulphatoxide of sodium or any other salt may be explained in the same simple manner; while on the other view, it must be assumed that a simultaneous transference between the electrodes of acid and alkali with the oxygen and hydrogen of water takes place; and the effect of the acid in promoting the decomposition of the water remains unaccounted for.

When a metallic oxide is dissolved in an acid solution, as oxide of zinc in diluted sulphuric acid, the reaction which occurs is thus explained on the binary theory:

Sulphatoxide of hydrogen.	{	Hydrogen . . .	-----	Water.
	{	Sulphatoxygen . . .	-----	
Oxide of zinc.	{	Oxygen . . .	-----	
	{	Zinc . . .	-----	Sulphatoxide of zinc;

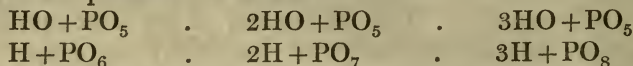
as in the reaction between the same oxide and hydrochloric acid (page 160).

The chief objections to the binary theory of salts, are—

First: The creation of so many hypothetical radicals; namely, one for every class of oxygen-acid salts. But it is to be remembered that the great proportion of oxygen acids, such as nitric, acetic, oxalic, &c. are equally of an ideal character and cannot be exhibited in a separate state.

Secondly: The peculiarities of the salts of phosphoric acid are supposed to be inimical to the new view. That acid forms three different and independent classes of salts, containing respectively one, two and three atoms of base to one of acid. On the binary theory, these three classes of salts must contain three different radicals, combined respectively with one, two

and three atoms of hydrogen or metal. The three phosphates of water and the corresponding phosphatoxides of hydrogen would be represented as follows :



Such radicals and such compounds with hydrogen startle us from their novelty, but it may be questioned whether they are really more singular than the anormal classes of phosphates, containing several atoms of base, for which they are substituted, but which we have been more accustomed to contemplate. All the salt-radicals known in a separate state, such as chlorine and cyanogen, combine with one atom only of hydrogen or metal, but it would be unfair to assume in the present imperfect state of our knowledge that other radicals may not exist, capable of combining with two or three atoms of metal, as the phosphate radicals are supposed to do. The existence of at least one such radical is highly probable, as will afterwards appear.

In conclusion, it may be stated that neither view of the constitution of the oxygen-acid salts, (which are alone affected by this discussion), rests on demonstrative evidence—they are both hypotheses and are both capable of explaining all the phenomena of the salts. But to whichever of them we give a preference, we can scarcely avoid using the language of the old theory in the present state of chemical science.

Without deciding definitively in favour of one or other of these views, a distribution of the great class of salts into three orders may be made. A certain number of salts contain radicals which can be isolated, others oxygen-acids which can be isolated, while others have yet afforded neither radical nor acid in a separate state. Hence, there are :

1. Salts of isolable radicals: chlorides, cyanides, sulphocyanides, &c.

2. Salts of isolable acids: sulphates, carbonates, &c.

3. Salts which contain neither an isolable radical nor an isolable acid: nitrates, acetates, hyposulphites, &c. Even admitting that all salts have the same constitution, the capability of breaking up in such different ways must affect their modes of decomposition in different circumstances, and produce distinctions in properties which would render such a division of them expedient.

It has become necessary to recognise three classes of oxygen-acid salts, which in the language of the old theory contain, one, two and three atoms of base to one of acid.

1. *Monobasic salts*.—The great proportion of acids, such as sulphuric, nitric, &c. neutralize but one atom of base, and form, therefore, *monobasic salts*. But this is not inconsistent with an acid's forming two series of salts with the same base or class of isomorphous bases. Thus there appear to be two well marked classes of sulphates of the magnesian oxides, which agree in having one atom of base, but differ essentially in the proportions of combined water which they affect. In one series the sulphate is combined with one, three, five or seven atoms of water. Copperas (a sulphate of iron), epsom salt (a sulphate of magnesia), blue vitriol (a sulphate of copper), and most of the well known magnesian sulphates belong to this class, which may be called the copperas class of sulphates. All the members of it are very soluble in water, and form double salts with sulphate of potash. The other series affect two, four and six atoms of water. They are less known, but appear to be of sparing solubility, and to be incapable of forming double salts with sulphate of potash. Gypsum or sulphate of lime belongs to this class, which may, therefore, be called the gypsum class of magnesian sulphates. Sulphate of iron crystallizes from solution in sulphuric acid with two atoms of water, with the crystalline form and sparing solubility of gypsum. Dr. Kane obtained a sulphate of copper with four atoms of water, by exposing the anhydrous salt to the vapour of hydrochloric acid, which appears to be the second term in this series; and Mitscherlich still maintains the existence of a peculiar sulphate of magnesia containing six atoms of water of crystallization, which will constitute the third term. It is evident that the cause of such double classes of salts is as deeply seated as that of dimorphism, and hence, possibly, the magnesian sulphate itself, which exists in the two classes, is not the same in its constitution with reference to heat.

2. *Bibasic salts*.—That class of phosphates, which received the name of pyrophosphates, was the only class of salts, known till lately, in which one atom of acid neutralizes two atoms of base. But according to the recent results of Fremy which have been favourably reported upon by Dumas,* the classes of tartrates

* L'Institut, May 1838, p. 141.

and racemates which have long been known to chemists, are also bibasic salts. It is the character of a bibasic acid to unite at once with two *different* bases, which accounts for the formation of Rochelle salt, the tartrate of potash and soda, of which the formula is $\text{KO}, \text{Na O} + \text{C}_8 \text{H}_4 \text{O}_{10}$. Liebig has also lately shown that gallic acid is bibasic,* the gallate of lead being thus composed $2\text{Pb O} + \text{C}_7 \text{H O}_3$. Now if we attempt to make this a monobasic salt by dividing the atoms both in base and acid by two, an atom of gallic acid would come to contain half an equivalent of hydrogen, which Liebig considers as conclusive against the division of its atomic weight. Lactic acid also is likely to prove bibasic.

3. *Tribasic Salts*.—The tribasic phosphates have proved to be the type of a class of salts. One atom of arsenic acid neutralizes three atoms of base; so, it is probable, does one atom of phosphorous acid. Tannic acid also saturates three atoms of base, the formula of the tannate of lead being $3\text{PbO} + \text{C}_{18} \text{H}_5 \text{O}_9$ (Liebig). There is the same necessity to admit that citric acid is tribasic, and the formula of a citrate $3\text{MO} + \text{C}_{12} \text{H}_5 \text{O}_{11}$, (in which M represents an atom of metal or of hydrogen) as there is to allow that gallic acid is bibasic. Most of the citrates contain two atoms of fixed base, and one of water, but the citrate of silver contains three atoms of oxide of silver. Cyanic, cyanuric and fulminic acids are isomeric, and all tribasic according to Liebig. The same chemist has also lately ascertained that the related acids, meconic, metameconic and pyromeconic, are respectively tribasic, bibasic and monobasic.†

Two of the three atoms of base in this class of salts may be different as is observed in certain citrates, cyanurates and phosphates, or the whole three may be different as in the phosphate called microcosmic salt, which contains at once soda, oxide of ammonium and water as bases.‡ Two or more of the bases may likewise be isomorphous, or at least belong to the same natural family as soda and oxide of ammonium, water and magnesia. This class and the last will probably be rapidly augmented by the addition of organic acids. Dumas considers it probable that the organic acids which are not volatile, like

* L'Institut, May 1838, page 141.

† Letter from M. Liebig, dated April 2, 1838.

‡ Inquiries respecting the constitution of salts; of oxalates, nitrates, phosphates, sulphates and chlorides. Phil. Trans. 1837, page 47.

tartaric and citric acids, have all a high atomic weight, which causes them to be fixed, and that the received equivalents of some of them may, therefore, require to be increased, which would afford room for viewing them as bibasic or tribasic.

Salts usually denominated Subsalts. The preceding classes of salts, and many other bodies also are capable of combining with a certain proportion of water, generally vaguely spoken of as water of crystallization. The compounds of the present class appear to be salts which have assumed a fixed metallic oxide in the place of this water. They may, therefore, be truly neutral in composition, the excess of oxide not standing in the relation of base to the acid. I have elsewhere shewn that crystallized nitrate of copper, nitrate of water, (acid of sp. gr. 1.42), and subnitrate of copper may be represented by the formulæ, $\text{CuO}, \text{NO}_5 + 3\text{HO}$; $\text{HO}, \text{NO}_5 + 3\text{HO}$; and $\text{HO}, \text{NO}_5 + 3\text{CuO}$, and have distinguished as *constitutional*, the three atoms of water which exist in these and all the magnesian nitrates, and which are replaced by three atoms of oxide of copper in the subnitrate of copper, which is, therefore, a nitrate of water with constitutional (not basic) oxide of copper, a view which is expressed by the arrangement of the symbols in its formula. Water, oxide of copper and oxide of lead appear to be the bodies most disposed to attach themselves to salts in this manner. The strong alkalies, potash and soda are never found in such a relation, or discharging any other function than that of base to the acid of the salt. These views of subsalts, in which their constitutional neutrality is preserved, have been adopted by Liebig and Dumas, and extended to organic compounds. Many neutral organic bodies appear to be capable of combining with metallic oxides particularly with oxide of lead, such as sugar, amidine, dextrine, orcine, and they generally combine with several atoms of the oxide; the neutral bodies mentioned being fixed and probably possessing a high atomic weight. Thus in the compound of orcine and oxide of lead, $\text{C}_{18} \text{H}_8 \text{O}_3 + 5\text{Pb O}$, the orcine must be present in the proportion of one atom, as the numbers of its constituent atoms have no common divisor; and the orcine, therefore, is combined with five atoms of constitutional oxide of lead, which actually replace five atoms of constitutional water which orcine otherwise contains.

Constitutional water is sometimes replaced by a *salt*, which

never happens with basic water. Thus starch or grape sugar, in its ordinary hydrated state, consists of $C_{12} H_{12} O_{12} + 2HO$; of which the two atoms of water may be replaced by chloride of sodium, and the compound formed, $C_{12} H_{12} O_{12} + 2NaCl$. It is to be observed that constitutional water is combined with a salt rather than in it, and such an element is removed and replaced without affecting the structure of the body to which it may be said to be attached. The replacing substance may also be a compound of a very different character from water, for besides metallic oxides and salts, ammonia and certain anhydrous acids appear to be capable of attaching themselves to salts, in the same manner as constitutional water.

Salts of the type of red chromate of potash. Several salts unite with anhydrous acids. Thus both chloride of sodium and chloride of potassium absorb and combine with two atoms of anhydrous sulphuric acid without decomposition, when exposed to the vapour of that substance. Sulphate of potash also combines with one atom of anhydrous sulphuric acid. All these compounds are destroyed by water. But the red chromate of potash, generally called bichromate of potash, which consists of chromate of potash together with one atom of chromic acid, is possessed of greater stability, as is likewise the compound of chloride of sodium or potassium with two atoms chromic acid. The red chromate might be viewed as a chromate of the chromate of potash, and the two last compounds as bichromates of the chlorides of potassium and sodium, but these expressions are more convenient than philosophical, and it will be safer in the present state of our knowledge to assimilate these salts in composition to the combinations of neutral bodies with constitutional water, particularly as we find the proportion of acid to be variable, and generally to be more than one atom. Thus a compound is known containing one atom of potash and three of chromic acid, which may be viewed as a combination of chromate of potash with two atoms of chromic acid, and represented by $KO, Cr O_3 + 2Cr O_3$. The red chromate of potash will then be $KO, Cr O_3 + Cr O_3$, and the chromate containing chloride of potassium, $KCl + 2Cr O_3$. The biniodate of potash (iodate of water and potash) may be rendered anhydrous, and while so, is a salt of this class.

Double Salts. Salts combine with each other, but by no

means indiscriminately. With a few exceptions which may be placed out of consideration for the present, the combining salts have always the same acid, sulphates combining with sulphates, chlorides with chlorides. Their bases or their metals, however, must belong to different natural families. Thus it may be questioned whether a salt of potash ever combines with a salt of soda, certainly never with a salt of ammonia. Salts of the numerous metals including hydrogen, belonging to the magnesian family, do not combine together; thus sulphate of magnesia does not form a double salt with sulphate of lime, with sulphate of zinc or with sulphate of water. While on the other hand salts of this family are much disposed to combine with salts of the potassium family; sulphate of soda, for instance, forming double salts with sulphate of lime, sulphate of zinc and sulphate of water. We have thus the means of distinguishing between a double salt, and the salt of a bibasic or tribasic acid. The bisulphate and binoxalate of potash, saturated with soda, form sulphates and oxalates of potash and soda, which separate from each other by crystallization, although the acid salts are themselves double salts of water and potash. But the acid fulminate of silver, or the acid tartrate of potash (bitartrate) affords only one salt when saturated with soda, in which isomorphous bases exist, and which, therefore, is a salt of one acid, and not a compound of two salts. The great proportion of the salts which are named *super*, *acid* and *bi*-salts, contain a salt of water and are double salts, such as the supercarbonate of soda ($\text{HO}, \text{CO}_2 + \text{NaO}, \text{CO}_2$), the acid sulphates of potash and the binacetate of soda; but a few of them are bibasic or tribasic salts, containing one or two atoms of water as base, such as the salt called bitartrate of potash, and biphosphate of potash ($2\text{HO}, \text{KO} + \text{PO}_5$).

There is no parallelism between the constitution of a double salt, and that of a simple salt itself, or foundation for the statements which are sometimes made, that one of the salts which compose a double salt has the relation to the other of an acid to a base, and that one salt is electro-negative to the other. The resolution of a double salt into its constituent salts by electricity, has never been exhibited, and is not to be expected from what is known of electrolytic action. While no analogy whatever subsists between a double salt and a simple salt on the binary view of the constitution of the latter. Besides, the

supposed analogy is destroyed by what is known of the derivation of double salts. Sulphate of magnesia acquires an atom of sulphate of potash in the place of an atom of water which is strongly attached to it, in becoming the double sulphate of magnesia and potash. In the same way, the sulphate of water has an atom of water also replaced by sulphate of potash, in becoming the bisulphate of potash; relations which appear in the rational formulæ of these salts:

Sulphate of magnesia	$\text{Mg } \ddot{\text{S}} (\dot{\text{H}}) + 6\dot{\text{H}}$
Sulphate of magnesia and potash	$\text{Mg } \ddot{\text{S}} (\ddot{\text{K}} \ddot{\text{S}}) + 6\dot{\text{H}}$
Sulphate of water (acid of sp. gr. 1.78)	$\dot{\text{H}} \ddot{\text{S}} (\dot{\text{H}})$
Bisulphate of potash	$\dot{\text{H}} \ddot{\text{S}} (\ddot{\text{K}} \ddot{\text{S}})$

It thus appears that a provision exists in sulphate of magnesia itself for the formation of a double salt, and that the molecular structure is unaltered, notwithstanding the assumption of the sulphate of potash as a constituent. The derivation of the acid oxalates likewise, throws much light on the nature of double salts. The oxalate of potash contains an atom of constitutional water, which is replaced by hydrated oxalic acid (the crystallized oxalate of water), in the formation of the binoxalate of potash (double oxalate of potash and water), or by the oxalate of copper in the formation of the double oxalate of potash and copper, as exhibited in the following formulæ, in which the replacing substances are enclosed in brackets to mark them as before:

Oxalate of potash	$\ddot{\text{K}} \ddot{\text{C}} \ddot{\text{C}} (\dot{\text{H}})$
Binoxalate of potash	$\ddot{\text{K}} \ddot{\text{C}} \ddot{\text{C}} (\dot{\text{H}} \ddot{\text{C}} \ddot{\text{C}} \dot{\text{H}}_2)$
Oxalate of potash and copper	$\ddot{\text{K}} \ddot{\text{C}} \ddot{\text{C}} (\ddot{\text{Cu}} \ddot{\text{C}} \ddot{\text{C}} \dot{\text{H}}_2)$

Now the anomalous salt, quadroxalate of potash, is derived in the same way from the binoxalate, as the binoxalate itself is derived from the neutral oxalate, two atoms of water being displaced by two atoms of hydrated oxalic acid, thus:

Binoxalate of potash	$\ddot{\text{K}} \ddot{\text{C}} \ddot{\text{C}}, \dot{\text{H}} \ddot{\text{C}} \ddot{\text{C}}, (2\dot{\text{H}})$
Quadroxalate of potash	$\ddot{\text{K}} \ddot{\text{C}} \ddot{\text{C}}, \dot{\text{H}} \ddot{\text{C}} \ddot{\text{C}}, (2\dot{\text{H}} \ddot{\text{C}} \ddot{\text{C}} \dot{\text{H}}_2)$

These examples illustrate the derivation of double salts by *substitution*. The structure of the salts too exemplifies what

may be called *consecutive* combination. The basis of the last mentioned salt, for instance, is oxalate of potash, which is in direct combination with oxalate of water. A compound body is thus produced which seems to unite *as a whole* with two atoms of hydrated oxalic acid. This is very different from the direct combination of all the elements which compose the salt.

In the formation of other classes of double salts, no substitution is observed, but simply the attachment of two salts together, often of an anhydrous with a hydrated salt, in which case the last often carries its combined water along with it, and sometimes acquires an additional proportion. Thus in the formula of the double chloride of potassium and copper, $K\ Cl + Cu\ Cl, 2HO$, the formulæ of its constituent salts reappear without alteration; and in that of alum, sulphate of potash is found with the hydrated sulphate of alumina annexed, of which the water is increased from eighteen to twenty-four atoms. In these and all other double salts, the characters of the constituent salts are very little affected by their state of union. If one of them has an acid reaction, like sulphate of alumina or chloride of copper, it retains the same character in combination; and nothing resembling a mutual neutralization of the salts by each other is ever observed.

The compounds of chlorides with chlorides, and of iodides with iodides are numerous, and were viewed by Bonsdorf as simple salts, in which one of the chlorides is the acid, and the other the base. But such an opinion can no longer be entertained, the chlorides themselves being unquestionably salts, and their compounds, therefore, double salts.

The combinations of such salts with each other as contain different acids are not so well understood, the theory of their formation having been little attended to. They are in general decomposed by water, and easily if the solubility of one of their constituents is considerable, as is observed of the compounds of iodate of soda with one and with two proportions of chloride of sodium, of the biniodate of potash with the sulphate of potash, of the oxalate of lime with the chloride of calcium.

The compound cyanides which form a considerable class of salts must be excepted from all the preceding general statements in regard to double salts. Cyanides of the same family combine together, as cyanide of iron with cyanide of hydrogen; the compound cyanide also generally consists of three and not of

two simple cyanides; and lastly the properties of compound cyanides are very different from those of the simple cyanides which are supposed to compose them. The simple cyanide of potassium, for instance, is highly poisonous, while the double cyanide of potassium and iron is as mild in its action upon the animal economy as sulphate of soda. But the compound cyanides may be removed from the class of double salts on a speculative view of their constitution, which their anomalous character warrants me in proposing. It is to be premised that the supposed double proto-cyanide of iron and potassium (yellow prussiate of potash) affords no hydrocyanic acid whatever when distilled with an excess of sulphuric acid at a temperature not exceeding 100° , which suggests the idea that it does not contain cyanides or cyanogen. Assuming the existence of a new compound radical, $N_3 C_6$, which has three times the atomic weight of cyanogen, and may be called *prussine*, and which is also *tribasic* or capable of combining with three atoms of hydrogen or metal, like the radical of the tribasic class of phosphates, then the compound cyanides assume a constitution of extreme simplicity. We have one atom of prussine combined always with three atoms of hydrogen or metal in the following salts; in the proto-cyanide of iron and potassium with one of iron and two of potassium; in the compound called ferro-cyanic acid, with one of iron and two of hydrogen; in Mosander's salts, with one of iron, one of potassium and one of barium, calcium, &c.; with two of iron and one of potassium in the salt which precipitates on distilling the yellow prussiate of potash with sulphuric acid at 212° . To many of these, parallel combinations might be adduced from the tribasic phosphates. Prussides likewise combine together, producing double prussides, such as:

Percyanide of iron and potassium

(red prussiate of potash)	$\cdot Fe_2, N_3 C_6 + K_3, N_3 C_6$
Prussian blue	$\cdot Fe_2, N_3 C_6 + Fe_3, N_3 C_6$
Basic prussian blue . . .	$\cdot Fe_2, N_3 C_6 + Fe_3, N_3 C_6 + Fe_2 O_3$

One of the proximate constituents in the class of salts, is always a metal or hydrogen on the one theory, or the oxide of a metal or of hydrogen on the other. The metal or the oxide in the salt is often spoken of as its radical, or the oxide of its radical, expressions which are perfectly correct, but apt to lead

to confusion from the application of the term "salt-radical" to the other constituent of the salt on the binary theory. It may be useful, therefore, to have a specific expression for the metallic radical of a salt, such as *basyle*, a term compounded of *base*, which is applied to the oxide of the metal, and *ἰλη*, *nature* or *principle*, a termination already adopted in particular cases in the sense here given to it. Thus of sulphate of soda, soda is the base and sodium the basyle; and on the binary theory, sulphatoxygen being the salt-radical, sodium is still the basyle of the same salt. But the necessity for such a term is chiefly occasioned by the extension which has been made by chemists of their views respecting saline combination to the compounds of ammonia, and to the great class of bodies called ethers, in which the existence of a compound basyle is recognized discharging the function of the simple metallic radical in ordinary salts.

Salts of Ammonia. Ammonia is a gaseous compound of one atom of nitrogen and three of hydrogen, of which the solution in water is caustic and alkaline, and which neutralizes acids perfectly, as potash and soda do. But all its oxygen-acid salts contain, besides ammonia, an atom of water which is essential to them, and inseparable without the destruction of the salt; and with this additional constituent, they are isomorphous with the salts of potash. Hydro-chloric acid also unites with ammonia without losing its hydrogen, and the compound or hydrochlorate of ammonia, which is isomorphous with the chloride of potassium, contains, therefore, an atom of hydrogen, besides chlorine and ammonia. Now, on the theory of these salts, the ammonia with this hydrogen or that of the water in the oxygen-acid salts, constitutes a hypothetical radical or basyle, *ammonium*, (NH_4) , to which allusion has already been made as being isomorphous with potassium. This view of the constitution of the salts of ammonia will be made obvious by a few examples.

ON THE AMMONIUM THEORY.

Hydrochlorate of ammonia, NH_3, HCl . Chloride of ammonium, NH_4, Cl .

Sulphate of ammonia, $\text{NH}_3 \text{HO}, \text{SO}_3$. Sulphate of oxide of ammonium, $\text{NH}_4 \text{O}, \text{SO}_3$.

Nitrate of ammonia, $\text{NH}_3 \text{HO}, \text{NO}_5$. Nitrate of oxide of ammonium, $\text{NH}_4 \text{O}, \text{NO}_5$.

The application of this theory to the compounds of ammonia with sulphuretted hydrogen and sulphur is particularly felicitous. These compounds may be thus represented, and placed in comparison with their potassium analogues, NH_4 being equivalent to K.

Sulphuret of ammonium	.	.	.	$\text{NH}_4 \text{ S}$.	KS
Hydrosulphuret of sulphuret of ammonium (bihydrosulphuret of ammonia)	.	.	.	$\text{NH}_4 \text{ S, HS}$.	KS, HS
Tritosulphuret of ammonium	.	.	.	$\text{NH}_4 \text{ S}_3$.	KS_3
Pentasulphuret of ammonium	.	.	.	$\text{NH}_4 \text{ S}_5$.	KS_5

Ammonium is supposed to present itself in a tangible form and in possession of metallic characters, in the formation of what is called the *ammoniacal amalgam*. When mercury alloyed with one per cent of sodium is poured into a saturated cold solution of sal ammoniac (chloride of ammonium), it undergoes a prodigious increase of bulk, increasing sometimes from one volume to two hundred volumes, without becoming in the least degree vesicular, and acquires a butyraceous consistence, while its metallic lustre is not impaired. A small addition is at the same time made to its weight, estimated at from 1 part in 2000 to 1 in 10,000, and which certainly consists of ammonia and hydrogen in the proportions of ammonium. The sodium, it is supposed, combines with the chlorine of chloride of ammonium, and the liberated ammonium with mercury, so that the metallic product is an amalgam of ammonium. It speedily resolves itself again spontaneously into running mercury, ammonia and hydrogen. But the change which occurs to the mercury in this experiment is of a recondite nature, and admits of, at least, one other hypothetical explanation which is equally probable. After all, however, neither isolation nor the metallic character is essential to ammonium as an alkaline radical, other basyles being now admitted, such as ethyle and benzoyle, which have no claim to such characters.*

Other classes of ammoniacal salts may be formed in which the fourth atom of hydrogen in ammonium is replaced by a metal of the magnesian family, and by copper in particular which most resembles hydrogen. Thus anhydrous chloride of copper absorbs an atom of ammonia with great avidity, which

* Viewed in relation with the organic basyles, it might be termed *ammonyle*, rather than ammonium.

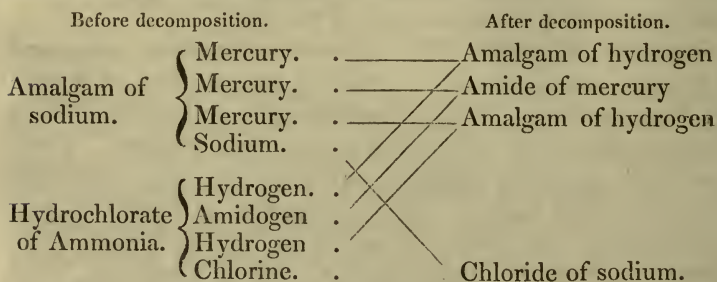
cannot afterwards be separated from it by the agency of heat. The compound is strictly analogous to chloride of ammonium, but contains an atom of copper in the place of hydrogen. Its formula is $\text{NH}_3 \text{Cu, Cl}$, and it may be named the chloride of *cuprammonium*. This salt and many others are likewise capable of combining with more ammonia, which is retained less strongly, and has the relation of constitutional water to the salt. The constitution of these combinations will be more minutely considered in another part of the work.

Amidogen and amides. The existence of another compound of nitrogen and hydrogen, containing an atom less of hydrogen than ammonia, (NH_2), is recognized in an important series of saline compounds, although it has not been isolated. These compounds are called *amides*, and hence the name amidogen applied to their radical. When potassium is heated in ammoniacal gas, the metal is converted into a fusible green matter, which appears to contain the amide of potassium, while an atomic proportion of hydrogen is disengaged. Amidogen exists also in the white precipitate of mercury of pharmacy, formed on adding ammonia to corrosive sublimate, the product being a double chloride and amide of mercury ($\text{Ag Cl} + \text{Hg NH}_2$). H

Amides are produced in an interesting way, by the abstraction of the elements of water from compounds of ammonia with oxygen acids. Thus, on decomposing oxalate of ammonia by heat, the acid losing a proportion of oxygen, and the ammonia a proportion of hydrogen, *oxamide* sublimes, which consists of $\text{NH}_2 + 2\text{CO}$. When ammoniacal gas and anhydrous sulphuric acid vapour are mixed together, a saline substance is produced which dissolves in water, but is not sulphate of ammonia, the solution affording no indications of sulphuric acid. It is believed to be a hydrated *sulphamide*, or to be constituted thus, $\text{NH}_2, \text{SO}_2 + \text{HO}$; a compound which it will be observed contains neither ammonia nor sulphuric acid. Similar products result from the action of ammonia on dry carbonic acid, and all the other anhydrous oxygen acids. The difference between these compounds and the true salts of ammonia affords a strong argument in favour of the ammonium theory of the latter.

The other speculative view of the constitution of the ammonical amalgam, to which allusion has been made, is suggested

by the remarkable and apparently peculiar aptitude of mercury to combine with amidogen, and by the position which hydrogen holds among elementary bodies, which is that of a *metal of the magnesian class*. It is, that the light ammoniacal amalgam is an amalgam of hydrogen, with the amide of mercury, or perhaps a double amide of mercury and chloride of sodium, diffused through it. The reaction by which these bodies may be produced, is explained in the following diagram :



Theory of the Ethers. As the ideas of chemists respecting salt-radicals first derived from certain simple bodies, such as chlorine, were afterwards extended through cyanogen, which so closely resembles them, to compound salt-radicals of greater complexity, so their ideas of basyles derived from the simple metals, have been extended through ammonium, which exhibits an absolute parallelism to potassium, to other compound basyles, the oxides and salts of which exhibit a less obvious relation to their metallic prototypes. In the theory of ether, first suggested by Berzelius, which was powerfully advocated by Liebig, and is now generally acquiesced in by chemists, that body is represented as the oxide of a basyle named *ethyle*, or as $C_4 H_5 O$; and is considered itself a true base capable of neutralizing acids, notwithstanding its want of alkalinity to the taste, or as tried by test-paper, although it is sapid and soluble in water. Alcohol, from the decomposition of which ether is derived, is the hydrate of the oxide of ethyle, $C_4 H_5 O, HO$; nitrous ether is the nitrite of ether, $C_4 H_5 O, NO_3$; oxalic ether, the oxalate of ether, $C_4 H_5 O, C_2 O_3$; and sulphovinic acid may be called either the bisulphate of ether, or the sulphate of water and ether, $HO, SO_3 + C_4 H_5 O, SO_3$. Hydrochloric ether is the chloride of ethyle, $C_4 H_5, Cl$. The same views are extended to all the compounds of ether with both oxygen and hydrogen acids.

Another class of saline compounds has been derived from wood-spirit, of which the basyle is *methyle*, $C_2 H_3 O$, equally numerous, and closely analogous in properties to the alcoholic series. Many other classes of organic compounds besides are found to correspond with that series, and the order of saline compounds is likely to undergo a vast expansion. It thus appears that conclusions respecting salts are of a wide and general application. Indeed the great question respecting the constitution of an oxygen-acid salt, is the pivot upon which the whole body of chemical theory turns at this moment.

SECTION II.

CHEMICAL AFFINITY.

In the preceding section, compound bodies have been viewed as already formed, and existing in a state of rest. The arrangement, weights and other properties of their atoms, have also been examined, with the relations and classification of the compounds themselves. But chemistry is more than a descriptive science; for it embraces, in addition to views of composition, the consideration of the action of bodies upon each other which leads to the formation and destruction of compounds. Certain bodies, when placed in contact, exhibit a proneness to combine with each other, or to undergo decomposition, while others may be mixed most intimately without change. The actual phenomena of combination suggest the idea of peculiar attachments and aversions subsisting between different bodies, and it was in this figurative sense that the term *affinity* was first applied by Boerhaave to a property of matter. A specific attraction between different kinds of matter must be admitted as the cause of combination, and this attraction may be conveniently distinguished as *chemical affinity*.

The particles of a body in the solid or liquid state exhibit an attraction for each other, which is the force of *cohesion*, and even different kinds of matter have often an attraction for each other, which is probably of the same nature, although distinguished as *adhesion*. This force retains bodies in contact, which are once placed in sufficient proximity to each other. It is exhibited in the adhesion of two smooth pieces of lead pressed together, or perfectly flat pieces of plate-glass, which

sometimes cannot again be separated. The action of glue, wax, mortar and other cements in attaching bodies together, depends entirely upon the same force. In detaching glue from the surface of glass, the latter is sometimes injured, and portions of it are torn off by the glue, the adhesive attraction of the two bodies being greater than the cohesion of the glass. The property of water to adhere to solid surfaces and wet them, its imbibition by a sponge, the ascent of liquids in narrow tubes, and other phenomena of capillary attraction, and the rapid diffusion of a drop of oil over the surface of water are illustrations of the same attraction between a liquid and a solid, and between different liquids. But this kind of attraction is deficient in a character which is never absent in true chemical affinity—*it effects no change in the properties of bodies*. It may bind different kinds of matter together, but it does not alter their nature.

The tendency of different gases to diffuse through each other till a uniform mixture is formed, is another property of matter, the effect of a force wholly independent of chemical affinity. It is certain that this physical property is not lost in liquids, and that it contributes to that equable diffusion of a salt through a menstruum which occurs spontaneously, and without agitation to promote it.*

Solution. The attraction between salt and water, which occasions the solution of the former, differs in several circumstances from the affinity which leads to the production of definite chemical compounds. In solution, combination takes place in indefinite proportions, a certain quantity of common salt dissolving in, or combining with any quantity of water however large; while a certain quantity of water, such as 100 parts can dissolve any quantity of that salt less than 37 parts, the proportion which saturates it. Water has a constant solvent power for every other soluble salt, but the maximum proportion of salt dissolved, or the saturating quantity, has no relation to the atomic weight of the salt, and indeed varies exceedingly with the temperature of the solvent. The limit to the solubility of a salt seems to be immediately occasioned by its cohesion. Water, in proportion as it takes up salt, has its power to disintegrate and dissolve more of the soluble body gradually diminished, it dissolves the

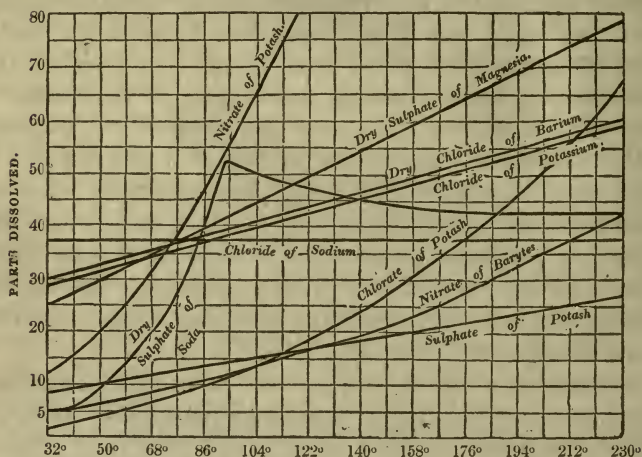
* Jerichau in Poggendorff's Annalen, 34, 613; or Dove and Moser's Repertorium der Physik, 1, 96. 1837.

last portions slowly and with difficulty, and at last when saturated is incapable of overcoming the cohesion of more salt that may be added to it. The solubility in water of another body in the liquid state is not restrained by cohesion, and is in general unlimited. Thus alcohol, and also soluble salts above the temperature at which they liquefy in their water of crystallization, dissolve in water in any proportion. Generally speaking also those salts dissolve in largest quantity which are most fusible, or of which the cohesion is most easily overcome by heat, as the hydrated salts, and among anhydrous salts, the nitrates, chlorates, chlorides and iodides which are all remarkable for their fusibility. In this species of combination, bodies are not materially altered in properties, indeed are little affected except in their cohesion.

The union also between a body and its solvent differs in a marked manner from proper chemical combination in the relation of the bodies to each other which exhibit it. Bodies *combine* chemically with so much the more force as their properties are more opposed, but they *dissolve* the more readily in each other, the more similar their properties. Thus metals combine with non-metallic bodies, acids with alkalis; but to dissolve a metal, another metal must be used, such as mercury; oxidated bodies dissolve in oxidated solvents as the salts and acids in water; while liquids which contain much hydrogen are the best solvents of hydrogenated bodies, an oil, for instance, of a fat or a resin, alcohol and ether dissolving the essential oils and most organic principles, but few salts of oxygen acids. The force which produces solution differs, therefore, essentially from chemical affinity in being exerted between analogous particles, in preference to particles which are very unlike, and resembles more, in this respect, the attraction of cohesion.

A more accurate idea of the varying solubility of a salt at different temperatures may be conveyed by a curve constructed to represent it, than by any other means. The perpendicular lines in the following diagram, indicate the degrees of temperature which are marked below them, and the horizontal lines, quantities of salt dissolved by 100 parts of water. The proportion of any salt dissolved at a particular temperature may be learned by carrying the eye along the perpendicular line, expressing that temperature, till it cuts the curve of the salt, and then horizontally to the column of parts dissolved.

SOLUBILITY OF SALTS IN 100 PARTS OF WATER.



It will be observed that the perpendicular lines advance by 9 degrees, the first being 32°, and the last 230°. The solubility of nitrate of potash increases from 13 parts in 100 water at 32°, to 80 parts at 118°, or very rapidly with the temperature. Sulphate of soda is seen by the form of its curve to increase in solubility from 5 parts at 32° to 52 parts at 92°, but then to diminish in solubility with farther elevation of temperature. In this salt, sulphate of magnesia and chloride of barium the solubility is expressed in parts of the anhydrous, and not the hydrated salt. The lines of chloride of barium and chloride of potassium are parallel, shewing a remarkable relation between the solubilities of these two salts, which does not appear in any others. The line of chloride of sodium is observed to cut all the lines of temperature at the same height, 100 parts of water dissolving 37 parts of that salt at all temperatures.

Chemical affinity acts only at insensible distances, and has no effect in causing bodies to approach each other, which are not in contact, differing in this respect from the attraction of gravitation which acts at all distances, however great, although with a diminishing force. Hence, the closest approximation of unlike particles is necessary to develop their affinities, and produce combination. Sulphur and copper in mass have no effect upon each other, but if both be in a state of great division, and rubbed together in a mortar, a powerful affinity is brought into play, the bodies themselves disappear, and sul-

phuret of copper is produced by their union, with the evolution of much heat. The affinity of bodies is, therefore, promoted by everything which tends to their close approximation; in solids, by their pulverization and intermixture, this attraction residing in the ultimate particles of bodies; in gases, by their spontaneous diffusion through each other, which occasions a more complete intermixture than is attainable by mechanical means; and between liquids, or between a liquid and solid by the adhesive attraction which liquids possess, which must lead to perfect contact, and also by a disposition of liquid bodies to intermix, of the same physical character as gaseous diffusion. Elevation of temperature has certainly often a specific action in increasing the affinity of two bodies, but it also often acts by producing a perfect contact between them, from the fusion or vaporization of one or both bodies. Hence, no practice is more general to promote the combination of bodies than to heat them together.

If the affinity between two gases is sufficiently great to begin combination, the process is never interrupted, but is continued from the diffusion of the gases through each other till complete, or at least till one of the gases is entirely consumed. Thus when hydrochloric acid and ammoniacal gases, in equal measures, are introduced into a jar containing at the same time a large quantity of air, the formation of hydrochlorate of ammonia proceeds, the gases appearing to search out each other, till no portion of uncombined gas remains. The combination of two liquids, or of a liquid and a solid, is also facilitated in the same manner by the mobility of the fluid, and proceeds without interruption, unless, perhaps, the product of the combination be solid, and by its formation interpose an obstacle to the contact of the combining bodies. But the affinities of two solids which are not volatile are rarely developed at all, owing to the imperfection of contact. Even the action of very powerful affinities between a solid and a liquid or a gas, is often arrested in the outset from the physical condition of the former. Thus, the affinity between oxygen and lead is certainly considerable, for the metal is rapidly converted into a white oxide, when ground to powder and agitated with water in its usual aerated condition; and in the state of extreme division in which lead is obtained by calcining its tartrate in a glass tube, the metal is a pyrophorus, and combines with oxygen

when cold with so much avidity as to take fire and burn the moment it is exposed to the air. Iron also, in the spongy and divided state in which it is procured by reducing the peroxide by means of hydrogen gas at a low red heat, absorbs oxygen with equal avidity at the temperature of the air, and takes fire and burns. But notwithstanding an affinity for oxygen of such intensity, these metals in mass oxidate very slowly in air, particularly lead, which is quickly tarnished indeed, but the thin coating of oxide formed does not penetrate to a sensible depth in the course of several years. The suspension of the oxidation may be partly due to the comparatively small surface which a compact body exposes to air, and which becomes covered by a coat of oxide and protected from farther change; but partly also to the effect of the conducting power of a considerable mass of metal in preventing the elevation of temperature consequent upon the oxidation of its surface. For metals oxidate with increased facility at a high temperature, such as the lead pyrophorus quickly attains from the oxidation of the great surface which it exposes, compared with its weight. The heat from the oxidation of the superficial particles of the compact metal, however, is not accumulated, but carried off and dissipated by the conducting power of the contiguous particles, so that elevation of temperature is effectually repressed. It thus appears that the state of aggregation of a solid may oppose an insuperable bar to the action of a very powerful affinity.

The affinity of two bodies, one or both of which are in the state of gas, is often promoted in an extraordinary manner by the contact of certain solid bodies. Thus oxygen and hydrogen gases may be mixed and retained for any length of time in that state without exhibiting any affinity for each other, and the gaseous mixture may, indeed, be heated in a glass vessel to any temperature short of redness without showing any disposition to combine. But if a clean plate of platinum be introduced into the cold mixture, the gases in contact with the metallic surface instantly unite and form water; other portions of the mixture come then in contact with the platinum and combine successively under its influence, so that a large quantity of the gaseous mixture may be quickly united. The temperature of the platinum also rises from the heat evolved by the combination occurring at its surface, and the influence of the metal in-

creasing with its temperature, combination proceeds at an accelerated rate, till the platinum becoming red hot, may cause the combination to extend to a distance from it, by kindling the gaseous mixture. Platinum acts in this manner with greatest energy when in a highly divided state, as in the form of spongy platinum, owing to the greater surface exposed and the rapidity with which it is heated. The metal itself contributes no element to the water formed, and is in no respect altered. It is an action of the metallic surface, which must be perfectly clean, and is retarded or altogether prevented by the presence of oily vapours and many other combustible gases, which soil the metallic surface. Mr. Faraday is disposed to refer the action to an adhesive attraction of the gases for the metal, under the influence of which they are condensed and their particles approximated within the sphere of their mutual attraction, so as to combine. This opinion is favoured by the circumstance that the property is not peculiar to platinum, but appears also in other metals, in charcoal, pounded glass, and all other solid bodies; although all of them, except the metals, act only when their temperature is above the boiling point of mercury. But on the other hand, at low temperatures, the property appears to be confined to a few metals only which resemble platinum in their chemical characters, namely in having little or no disposition to combine with oxygen gas, and in not undergoing oxidation in the air. The action of platinum may, therefore, be connected with its chemical properties, although in a way which is quite unknown to us. The same metal disposes carbonic oxide gas to combine with oxygen, but much more slowly than hydrogen; and it is remarkable that if the most minute quantity of carbonic oxide be mixed with hydrogen, the oxidation of the latter under the influence of the platinum is arrested, and not resumed till after the carbonic oxide has been slowly oxidated and consumed, which thus takes the precedence of the hydrogen in combining with oxygen. This extraordinary interference of a minute quantity of carbonic oxide gas, which cannot from its nature be supposed to soil the surface of the platinum like a liquefiable vapour, seems to point to a chemical, perhaps to an electrical explanation of the action of the platinum, rather than to the adhesive attraction of the metal. The oxidation of alcohol at the temperature of the air, and also at a low red heat, is promoted in the same manner by contact with platinum.

Order of affinity. The affinity between bodies appears to be of different degrees of intensity. Lead, for instance, has certainly a greater affinity than silver for oxygen, the oxide of the latter being easily decomposed when heated to redness, while the oxide of the former may be exposed to the most intense heat without losing a particle of oxygen. Again, it may be inferred that potassium has a still greater affinity for oxygen than lead possesses, as we find the oxide of lead easily reduced to the metallic state when heated in contact with charcoal, while potash is decomposed in the same manner with great difficulty. But the order of affinity is often more strikingly exhibited in the decomposition of a compound by another body. Thus sulphuretted hydrogen gas is decomposed by iodine, which combines with the hydrogen forming hydriodic acid, and liberates sulphur. The affinity of iodine for hydrogen is, therefore, greater than that of sulphur for the same body. But hydriodic acid is deprived of its hydrogen by bromine, and hydrobromic acid is formed; and this last is decomposed in its turn by chlorine, and hydrochloric acid produced. It thus appears that the order of the affinity of the elements mentioned *for hydrogen* is, chlorine, iodine, bromine, sulphur. The order of decompositions, in the precipitation of metals by each other from their saline solutions, also indicates the degree of affinity. Thus from the decomposition of the nitrates of the following metals, the order of their affinity *for nitric acid and oxygen* may be inferred to be as follows: zinc, lead, copper, mercury, silver; zinc throwing down lead from the nitrate of lead, and all the other metals which follow it, lead throwing down copper; copper, mercury; and mercury, silver; while nitrate of zinc itself is not affected by any other metal, and nitrate of silver is decomposed by all the metals enumerated. Bodies were first thus arranged according to the degree of their affinity for a particular substance, inferred from the order of their decompositions, by Geoffroy and Bergman, and tables of affinity constructed of which the following is an example. Order of affinity of the alkalis and earths *for sulphuric acid*.

Barytes
Strontian
Potash
Soda
Lime
Magnesia
Ammonia

Barytes is capable of taking sulphuric acid from strontian, potash and every other base which follows it in the table, the experiment being made upon sulphates of these bases dissolved in water; while sulphate of barytes is not decomposed by any other base. Lime separates ammonia and magnesia from sulphuric acid, but has no effect upon the sulphates of soda, potash, strontian and barytes; and in the same manner any other base decomposes the sulphates of the bases below it in the column, but has no effect upon those above it. Tables of this kind when accurately constructed may convey much valuable information of a practical kind, but it is never to be forgotten that they are strictly tables of the order of decomposition and of the comparative force or order of affinity in one set of conditions only. This will appear by examining how far decomposition is affected by accessory circumstances in a few cases.

Circumstances which affect the order of decomposition. Volatility in a body promotes its separation from others which are more fixed, and consequently facilitates the decomposition of compounds into which the volatile body enters. Hence, by the agency of heat, water is separated from hydrated salts; ammonia, from its combinations with a fixed acid, such as the phosphoric; and a volatile acid from many of its salts, as sulphuric acid from the sulphate of iron, carbonic acid from the carbonate of lime, &c. Ammonia decomposes hydrochlorate of morphia at a low temperature, but on the other hand, morphia decomposes the hydrochlorate of ammonia at the boiling point of water, and liberates ammonia, owing to the volatility of that body. The fixed acids, such as the silicic and phosphoric disengage in the same way at a high temperature those acids which are generally reputed most powerful, and by which silicates and phosphates are decomposed with facility at a low temperature. Many such cases might be adduced in which the order of decomposition is reversed by a change of temperature. The volatility of one of its constituents must, therefore, be considered an element of instability in a compound.

Decomposition from unequal volatility is, of course, checked by pressure, and promoted by its removal and by every thing which favours the escape of vapour, such as the presence of an atmosphere of a different sort into which the volatile constituent may evaporate. Carbonate of lime is decomposed easily at a

red heat, provided a current of air or of steam is passing over it which may carry off the carbonic acid gas, but the decomposition ceases when the carbonate is surrounded by an atmosphere of its own gas; and the carbonate may even be heated to fusion, in the lower part of a crucible, without decomposition. Here the occurrence of decomposition depends entirely upon the existence of a foreign atmosphere into which carbonic acid can diffuse. Nitrates of alumina and peroxide of iron in solution, are decomposed by the spontaneous evaporation of their acid, even at the temperature of the air; and so is an alkaline bicarbonate when in solution, but not when dry. A change in the composition of the gaseous atmosphere may affect the order of decomposition as in the following cases:

When steam is passed over iron at a red heat a portion of it is decomposed, oxide of iron being formed and hydrogen gas evolved. From this experiment it might be inferred that the affinity of iron for oxygen is greater than that of hydrogen. But let a stream of hydrogen gas be conducted over oxide of iron at the very same temperature, and water is formed, while the oxide of iron is reduced to the metallic state. Here the hydrogen appears to have the greater affinity for oxygen. But the result is obviously connected with the relative proportion between the hydrogen and steam which are at once in contact with the metal and its oxide at a red heat. When steam is in excess, water is decomposed, but when hydrogen is in excess, oxide of iron is decomposed; and why, because the excess of steam in the first case is an atmosphere into which hydrogen can diffuse, and the disengagement of that gas is therefore favoured; but in the second case the atmosphere is principally hydrogen, and represses the evolution of more hydrogen, but facilitates that of steam. The affinity of iron and hydrogen for oxygen at the temperature of the experiment, is so nearly balanced that the one affinity prevails over the other, according as there is a proper atmosphere into which the gaseous product of its action may diffuse. This affords an intelligible instance of the influence of mass or quantity of material, in promoting a chemical change; the steam or the hydrogen, as it preponderates, exerting a specific influence, in the capacity of a gaseous atmosphere.

The remarkable decomposition of alcohol by sulphuric acid, which affords ether, is another similar illustration of decom-

position depending upon volatility, and affected by changes in the nature of the atmosphere into which evaporation takes place. Alcohol or the hydrate of ether is added in a gradual manner to sulphuric acid somewhat diluted, and heated to 280° . In these circumstances, the double sulphate of ether and water is formed; water, which was previously combined as base to the acid, being displaced by ether, and evolved together with the water of the alcohol. The first effect of the reaction therefore, is the disengagement of watery vapour, and the creation of an atmosphere of that substance which tends to check its farther evolution. But the existence of such an atmosphere offers a facility for the evaporation of ether, which accordingly escapes from combination with the acid and continues to be replaced by water, the affinity of sulphuric acid for water and for ether being nearly equal, till ether forms such a proportion of the gaseous atmosphere as to check its own evolution, and to favour the evolution of watery vapour. Then again alcohol is decomposed, and more of the double sulphate of water and ether formed as at first; the sulphate of ether of which comes in its turn to be decomposed as before, and ether evolved. Hence, both ether and water distil over in this process, the evolution of one of these bodies favouring the separation and disengagement of the other. In this description, the evolution of water and ether are for the sake of perspicuity supposed to alternate, but it is evident that the result of such an action will be the simultaneous evolution of the two vapours in a certain constant relation to each other.

Influence of insolubility. The great proportion of chemical reactions which we witness are exhibited by bodies dissolved in water or some other menstruum, and are affected to a great extent by the relations of themselves and their products to their solvent. Thus carbonate of potash dissolved in water is decomposed by acetic acid, and carbonic acid evolved, the affinity of the acetic acid prevailing over that of the carbonic acid for potash. But if a stream of carbonic acid gas be sent through acetate of potash dissolved in alcohol, acetic acid is displaced, or the carbonic acid prevails, apparently from the insolubility of the carbonate of potash in alcohol. The insolubility of a body appears to depend upon the cohesive attraction of its particles, and such decompositions may therefore be ascribed to the prevalence of that force.

in which the constituents of both salts before decomposition inclosed in brackets, are found to have exchanged places after decomposition, without any other change in the original salts.* The double sulphate of lime and soda can be formed artificially only in circumstances, which are somewhat similar. It is produced on adding sulphate of soda to acetate of lime, the sulphate of lime, as it then precipitates, carrying down sulphate of soda in the place of constitutional water (Liebig).

Different hydrates of the same body such as peroxide of tin, differ sensibly in properties, and afford different compounds with acids, unquestionably because these compounds are formed by substitution. The constant formation of phosphates containing one, two or three atoms of base, on neutralizing the corresponding hydrates of phosphoric acid with a fixed base, likewise illustrates in a striking manner the derivation of compounds, on this principle. Many insoluble substances, such as the earth silica, possess a larger proportion of water, when newly precipitated, than they retain afterwards, and in that high state of hydration they may exhibit affinities for certain bodies which do not appear in other circumstances. Hydrated silica dissolves in water at the moment of its separation from a caustic alkali; and alumina dissolves readily in ammonia, when produced in contact with that substance by the oxidation of aluminum. The unusual disposition to enter into combination which silica and alumina then exhibit is generally ascribed to their being in the *nascent state*, a body at the moment of its formation and liberation, in consequence of a decomposition, being, it is supposed in a favourable condition to enter anew into combination. But their degree of hydration in the nascent state may be the real cause of their superior aptitude to combine.

Double decompositions take place without the great evolution of heat, which often accompanies the direct combination of two bodies, and with an apparent facility or absence of effort, as if the combinations were just balanced by the decompositions, which occur at the same time. It is perhaps from this cause that the result of double decomposition is so much affected by circumstances, particularly by the insolubility of one of the compounds. For it is a general law to which there is no exception, that two soluble salts cannot be mixed without the occur-

* On water as a constituent of sulphates, Phil. Mag. 3d series, vol. VI. p. 417.

rence of decomposition, if one of the products that may be formed is as insoluble salt. On mixing carbonate of soda and nitrate of lime, the decomposition seems to be determined entirely by the insolubility of the carbonate of lime, which precipitates. When sulphate of soda and nitrate of potash are mixed, no visible change occurs, and it is doubtful whether the salts act upon each other, but if the mixed solution be concentrated, decomposition occurs and sulphate of potash separates by crystallization owing to its inferior solubility.

It may sometimes be proved that double decomposition occurs on mixing soluble salts, although no precipitation supervenes. Thus on mixing strong solutions of sulphate of copper and chloride of sodium, the colour of the solution changes from blue to green, which indicates the formation of chloride of copper, and consequently that of sulphate of soda also. Now it is known that hydrochloric acid will displace sulphuric acid from the sulphate of copper, at the temperature of the experiment, while sulphuric acid will on the other hand displace hydrochloric from chloride of sodium. It hence appears that in the preceding double decomposition, those acids and bases unite which have the strongest affinity for each other, and the same thing may happen on mixing other salts. But where the order of the affinities for each other of the acids and bases is unknown, the occurrence of any change upon mixing salts, or the extent to which the change proceeds, is entirely matter of conjecture.

It was the opinion of Berthollet, founded principally upon the phenomena of the double decompositions of salts, that decompositions are at all times dependent upon accidental circumstances, such as the volatility or insolubility of the product, and never result from the prevalence of certain affinities over others; and consequently that in accounting for such changes, the consideration of affinity may be neglected. He supposed that when a portion of base is presented at once to two acids, it is divided equally between them, or in the proportion of the quantities of the two acids, and that one acid can come to possess the base exclusively, only when it forms a volatile or an insoluble compound with that body, and thereby withdraws it from the solution and from the influence of the other acid. His doctrine will be most easily explained by applying it to a particular case, and expressing it in the language of the atomic theory. The reaction

between sulphuric acid and nitrate of potash is supposed to be as follows. On mixing eight atoms of the acid with the same number of atoms of the salt, the latter immediately undergoes partial decomposition, its base being equally shared between the two acids which are present in equal quantities; and a state of statical equilibrium is attained in which the bodies in contact are :

(a) Four atoms sulphate of potash.

Four atoms nitrate of potash.

Four atoms sulphuric acid.

Four atoms nitric acid.

The nitrate of potash, it is supposed, is decomposed to the extent stated, and no farther, however long the contact is protracted. But let the whole of the free nitric acid now be removed by the application of heat to the mixture, and a second partition of the potash of the remaining nitrate of potash is the consequence; the free sulphuric acid decomposing the salt till the proportion of the two acids uncombined in the mixture is again equal, when a state of equilibrium is attained. The mixture then consists of :

(b) Six atoms sulphate of potash.

Two atoms nitrate of potash.

Two atoms sulphuric acid.

Two atoms nitric acid.

On removing the free nitric acid as before, a third partition of the potash of the remaining nitrate of potash, between the two acids, on the same principle takes place, of which the result is :

(c) Seven atoms sulphate of potash.

One atom nitrate of potash,

One atom of sulphuric acid.

One atom nitric acid.

The proportion of the two acids, free, being always the same. The repeated application of heat, by removing the free nitric acid, will cause the sulphuric to be again in excess, which will necessitate a new partition of the potash of the remaining nitrate of potash, till at last the entire separation of the nitric acid will be effected, and the fixed product of the decomposition be :

(d) Eight atoms sulphate of potash.

Here the affinity of the sulphuric and nitric acids, for potash is supposed to be equal; and the complete decomposition of the nitrate of potash by the former acid which takes place, is ascribed to the volatility of the latter acid, which, by occasioning its removal in proportion as it is liberated, causes the fixed sulphuric acid to be ever in excess.

Complete decompositions in which the precipitation of an insoluble substance occurs, were explained by Berthollet in the same manner. On adding a portion of barytes to sulphate of soda, the barytes decomposes the salt, and acquires sulphuric acid, till that acid is divided between the two bases in the proportion in which they are present, and, at this point, decomposition would cease, were it not that the whole sulphate of barytes formed, is removed by precipitation. But a new formation of that salt is the necessary consequence of that equable partition of the acid between the two bases in contact with it, which is the condition of equilibrium; and the new product precipitating, more and more of it is formed, till the sulphate of soda is entirely decomposed, and its sulphuric acid removed by an equivalent of barytes.

According to these views of Berthollet, no decomposition should be complete, unless the product be volatile or insoluble, as in the cases instanced. But such a conclusion is not consistent with observation, as it can be shewn that a body may be separated completely from a compound, and supplanted by another body, although none of the products is removed by the operation of either of the causes specified, but all continue in solution and in contact with each other. Thus the salt borax, which is a borate of soda, is entirely decomposed by the addition to its solution of a quantity of sulphuric acid, not more than equivalent to its soda, although the liberated boracic acid remains in solution; for the liquid imparts to blue litmus paper a purple or wine-red tint, which indicates free boracic acid, and not that characteristic red tint, resembling the red of the skin of the onion, which would inevitably be produced by the most minute quantity of the stronger acid, if free. But if the borax were only decomposed in part in these circumstances, and its soda equally divided between the two acids, then free sulphuric, as well as boracic acid, should be found in the solution. The complete decomposition of the salt can

be accounted for in no way but by ascribing it to the higher affinity of sulphuric acid for soda, than that of boracic acid for the same base.

According to the same views, on mixing together two neutral salts containing different acids and bases, and which do not precipitate each other, each acid should combine with both bases, so as to occasion the formation of four salts. Again, four salts, of which the acids and bases are all dissimilar, should react upon each other in such a way as to produce sixteen salts, each acid acquiring a portion of the four bases; and certain acids and bases, dissolved together in certain proportions, could have but one arrangement in which they would remain in equilibrio. Hence the salts in a mineral water would be ascertained by determining the acids and bases present, and supposing all the bases proportionally divided among the acids. But this conclusion is inconsistent with a fact observed in the preparation of factitious mineral waters, namely, that their taste depends not only on the nature of the salts, but also upon the order in which they are added, (Dr. Struve of Dresden.) Before we can determine how the acids and bases are arranged in a mineral water, or what salts it contains, it may therefore be necessary to know the history of its formation. Instead of supposing the bases equally distributed among the acids in mixed saline solutions, it is now more generally assumed that the strongest base may be exclusively in possession of the strongest acid, and the weaker bases be united with the weaker acids, a mode of viewing their composition which agrees best with the medical qualities of mineral waters. It thus appears that the doctrines of Berthollet, by which the resulting actions between bodies in contact are made to depend upon their relative quantities or masses and the physical properties of the products of their combination, to the entire exclusion of the agency of proper affinities between the bodies in contact, cannot be admitted as a true representation of the actual phenomena of combination.

CATALYSIS, OR DECOMPOSITION BY CONTACT.

An interesting class of decompositions has of late attracted considerable attention, which, as they cannot be accounted for on the ordinary laws of chemical affinity, have been referred by Berzelius to a new power, or rather new form of the force

of chemical affinity, which he has distinguished as the *Catalytic force*, and the effect of its action as *Catalysis* (from *kata* downwards, and *λυω*, I unloosen). A body in which this power resides, resolves others into new compounds, merely by contact with them, or by an action of presence, as it has been termed, without gaining or losing anything itself. Thus an acid converts a solution of starch (at a certain temperature), first into gum, and then into sugar of grapes, although no combination takes place between the elements of the acid, and those of the starch, the acid being found free and undiminished in quantity, after effecting the change. The same mutations are produced in a more remarkable manner by the presence of a minute quantity of a vegetable principle *diastase*, allied in its general properties to gluten, which appears in the germination of barley and other seeds, and converts their starch into sugar and gum, which being soluble, form the sap that rises into the germ, and nourishes the plant. This example of the action of a catalytic power in an organic secretion is probably not the only one in the animal and vegetable kingdoms, for it is not unlikely that it is by the action of such a force that very different substances are obtained from the same crude material by different organs. In animals this crude material, which is the blood, flows in the uninterrupted vessels, and gives rise to all the different secretions; such as milk, bile, urine, &c. without the presence of any foreign body which could form new combinations. A beautiful instance of an action of catalysis has been traced by Liebig and Wöhler in the chemical changes which the bitter almond exhibits. The application of heat and water to the almond, by giving solubility to its emulsin or albuminous principle, enables it to act upon an associated principle, amygdalin, of a neutral character, which then furnishes bodies so unlike itself as the volatile oil of almonds, and the hydrocyanic, oxalic and formic acids. The action of yeast in fermentation is a more familiar illustration of a similar power. The presence of that substance, although insoluble, is sufficient to cause the resolution of sugar into carbonic acid gas and alcohol, a decomposition which can be effected by no other known means. Changes of this kind, although most frequent in organic compounds, are not confined to them. The peroxide of hydrogen, discovered by Thenard, is a body of which the elements are

held together by a very slight affinity. It is not decomposed by acids, but alkalies give its elements a tendency to separate, slow effervescence occurring with the disengagement of oxygen, and water being formed. Nor do soluble substances alone produce this effect; other organic and inorganic bodies, also, such as manganese, silver, platinum, gold, fibrin, &c. which are perfectly insoluble, exert a similar power. The decomposition, in these instances, takes place by the mere presence of the foreign body, and without the smallest quantity of it entering into the new compound, for the most minute researches have failed in discovering the slightest alteration in the foreign body itself. The liquid persulphuret of hydrogen, and a solution of the nitrosulphate of ammonia of Pelouze are decomposed in the same way, and by contact of nearly all the substances which act upon peroxide of hydrogen. One remarkable difference indeed is observable, namely that alkalies impart stability to nitrosulphate of ammonia, while acids decompose it, or the reverse of what happens with both the peroxide and persulphuret of hydrogen.*

The phenomena referred to catalysis are of a recondite nature and much in need of elucidation. The influence of platinum, formerly noticed, in disposing hydrogen and oxygen to unite, is probably connected with the catalytic power of the same metal, but is at present equally inexplicable. It would be unphilosophical to rest satisfied by referring such phenomena to a force, of the existence of which we have no evidence. The doctrine of catalysis must be viewed in no other light than as a convenient fiction, by which we are enabled to class together a number of decompositions not provided for in the theory of chemical affinity as at present understood, but which, it is to be expected, will receive their explanation from new investigations. It is a provisional hypothesis, like the doctrine of isomerism, for which the occasion will cease as the science advances.

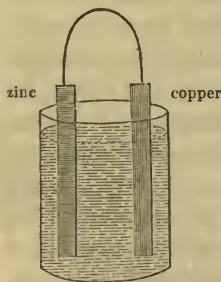
INDUCTIVE AFFINITY.

When a plate of zinc is plunged into hydrochloric acid, a chemical change of a simple nature ensues, the metal dissolves combining with the chlorine of the acid and displacing its hydrogen, the gas-bubbles of which form upon the zinc plate, increase in size, detach themselves, and rise through the liquor to its surface. The solution of zinc, when effected by its

* Phil. Mag. 3rd Series, vol. 10, p. 489.

substitution for hydrogen, as in this experiment, is attended by a train of extraordinary phenomena, which become apparent when a second metal, such as copper, silver, or platinum is placed in the same acid fluid, and allowed to touch the zinc, the second metal being one upon which the fluid exerts no solvent action, or a less action than upon zinc.

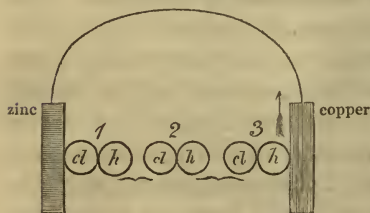
FIG. 1.



The zinc plate being connected by a metallic wire with a copper plate, as represented in the figure, and both dipped together in the hydrochloric acid, the zinc only is acted upon, and dissolves as rapidly as before; but much of the hydrogen gas now appears upon, and is discharged from the surface of the copper plate, and not from the zinc. The hydrogen, being produced by the solution of the zinc, thus appears to travel through the liquid from that metal to

the copper. But no current or movement in the liquid is perceptible, nor any phenomenon whatever to indicate the actual passage of matter through the liquid in that direction. The transference of the hydrogen must take place by the propagation of a decomposition through a chain of particles of hydrochloric acid extending from the zinc to the copper, and may be conceived by the diagram on the margin, in which

FIG. 2.

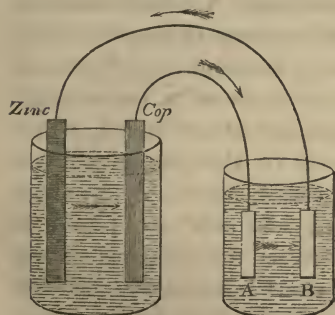


each pair of associated circles marked *cl* and *h* represents a particle of hydrochloric acid. The chlorine *cl* of particle 1 in contact with the zinc combining with that metal, its hydrogen *h* combines, the moment it is set free, with the chlorine of particle 2, as indicated by the connecting bracket below, and liberates the hydrogen of that particle, which hydrogen forthwith combines with the chlorine of particle 3, and so on through a series of particles of any extent till the decomposition reaches the copper plate, when the last liberated atom of hydrogen (that of particle 3 in the diagram) not having hydrochloric acid to act upon, is evolved and rises as gas in contact with the copper plate.

It is to be observed that this succession of decompositions and recombinations leading to the discharge of the hydrogen at

the copper, does not occur at all unless that plate be in metallic connexion with the zinc, by means of a wire as in the figure, or by the plates themselves touching without or within the acid fluid. This would seem to indicate that while the decomposition travels from the zinc to the copper through the acid, some force or influence is propagated at the same time through the wire, from the copper back again to the zinc. That something does pass through the wire in these circumstances is proved by its being heated, and by its temporary assumption of certain electrical and magnetic properties. Whether anything material does pass, or it is merely a vibration or vibratory impulse, or a certain induced condition that is propagated through the molecules of the wire, of which the electrical appearances are the effects, cannot be determined with certainty. But a power to effect decomposition, the same in kind as that occurring in the acid jar, and which acts in the same sense or direction, is propagated through the wire, and appears to be fundamental to all the other phenomena.

FIG. 3.



Let the wire, supposed to be of platinum, connecting the zinc and copper plates, be divided in the middle, and the extremities A and B of the portions attached to the copper and zinc plates respectively be flattened into small plates, and then dipped at a little distance from each other in a second vessel containing hydriodic acid. Iodine will soon appear at A, although that element is incapable of combining with the substance of the platinum, and hydrogen gas will appear at B. If the connecting wire and the small plates A and B were of zinc or of copper, the hydriodic acid would be decomposed precisely in the same manner, but the iodine as it reached A would unite with the metal and form an iodide. Supposing a decomposing force to have originated in the zinc plate, and to have circulated through the hydrochloric acid in the jar to the copper plate, and onwards through the wires and the hydriodic acid back to the zinc, as indicated by the direction of the arrows, then the hydrogen of the hydriodic acid has followed the same course, and been discharged against the metallic surface to which the arrow points.

The solution of the zinc in hydrochloric acid which develops these powers, acting at a distance, is not itself impeded, but on the contrary, is promoted by exerting such an influence. For placed alone in the acid, that metal scarcely dissolves at all, if pure and uncontaminated with other metals, or if its surface has been silvered with mercury, but it dissolves with rapidity when a copper plate is associated with it in the same jar, in the manner described. Hence the decomposing power which appears between A and B, cannot be viewed as actually a portion of that which causes the solution of the zinc in the hydrochloric acid, for that force has suffered no diminution in its own proper sphere of action.

This combination of metals and fluids is known as the *simple voltaic circle*.

To explain the phenomena of the voltaic circle, the existence of a substantial principle, the electric fluid, has been assumed, of such a nature that it is readily communicable to matter, and capable of circulating through the voltaic arrangement, carrying with it peculiar attractive and repulsive forces which occasion the decompositions observed. A vehicle was thus created for the chemical affinity which is found to circulate. But it is generally allowed that this form of the electrical hypothesis has not received support from observations of a recent date, particularly from the great discoveries of Mr. Faraday, which have completely altered the aspect of this department of science, and suggest a very different interpretation of the phenomena. All electrical phenomena whatever are found to involve the presence of matter, or there is no evidence of the independent existence of electricity apart from matter, so that these phenomena may really be exhibitions of the inherent properties of matter. The idea of anything like a circulation of electricity through the voltaic circle appears to be abandoned. Electrical induction, by which certain forces are propagated to a distance, is found to be always an action of contiguous particles upon each other, in which it is unnecessary to suppose that anything passes from particle to particle, or is taken from one particle and added to another. The change which a particle undergoes, takes place within itself, and it is looked upon as a temporary development of different powers in different points of the same particle. The doctrine of polarity has thus come to be introduced into the discussion of electrical phenomena.*

* For Mr. Faraday's more recent views, the Eleventh and subsequent series of

One reason for retaining the theory of an electrical fluids, is that it affords the means of expressing in terms those strictly physical laws, which are reputed electrical; and for many purposes such an hypothesis is unquestionably useful, if not absolutely necessary; but it has nothing to recommend it in the description of the chemical phenomena of the voltaic circle. These admit of a perfectly intelligible statement, when viewed as an exhibition of ordinary chemical affinity, acting in particular circumstances, without any electrical hypothesis. It is often said that chemical affinity acts only at insensible distances, and this may be true of its direct action, but is not inconsistent with its exerting an influence at a distance, like many other forces, *by an inductive agency*, a mode of action which requires careful consideration.

Magnetical polarity.—The ideas of induction and polarity, which now play so important a part in physical theories, were originally suggested by the phenomena of magnetism, which still afford the best illustrations of them. A bar magnet exhibits attractive power which is not possessed in an equal degree by every particle composing the bar, but is chiefly localized in two points at or near its extremities. The powers, too, residing at these points are not one and the same, or similar, but different, indeed contrary in their nature; and are distinguished by the different names of Boreal magnetism and Austral magnetism. The opposition in the mode of action of these powers is so perfect, that they completely neutralize each other when residing in the same particle of matter in equal quantity or degree, as they are supposed really to exist in iron before it is magnetized; and they only signalize their presence when displaced and separated to a distance from each other, as they are in a magnet. A body possessing any such powers residing in it, which are not general, but local, and not the same, but opposite, is said (in the most general sense) to possess *polarity*.

In the theory of magnetism, it is found necessary to consider a magnet as composed of minute, indivisible particles or

his Researches in the Philosophical Transactions for 1836, and the following years, may be referred to. He has lately favoured the scientific world with a reprint of the whole series: 'Faraday's Experimental Researches in Electricity, R. and J. E. Taylor, London, 1839. The subject is also systematically treated by Professor Daniell in his recent work, An Introduction to the Study of Chemical Philosophy, which may be consulted with advantage.

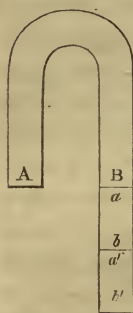
filaments of iron, each of which has individually the properties of a separate magnet. The displacement or separation of the two attractive powers takes place only within these small particles, which are called the magnetic elements, and must be supposed so minute, that they may be the ultimate particles or atoms themselves of the iron. A magnetic bar may therefore

FIG. 4.

be represented (as in the figure) as composed of minute portions, the right hand extremities of each of which possess one

species of magnetism, and the left hand extremities the other. The shaded ends being supposed to possess boreal, and the light ends austral magnetism, then the ends of the bar itself, of which these sides of the elementary magnets form the faces, possess respectively boreal and austral magnetism, and are the boreal and austral poles of the magnet. Such, then, is the polarized condition of a bar of iron possessing magnetism, of which the attractive and repulsive powers residing at the extremities are the results. Of the existence of such a structure, the breaking of a magnet into two or more parts affords a proof, for it forms as many complete magnets as there are parts, new poles appearing at all the fractured extremities.

FIG. 5.

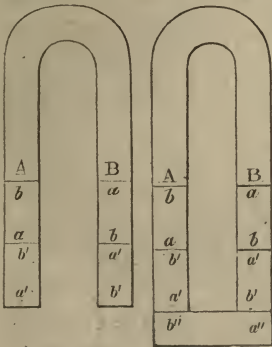


Magnetical induction.—When to the boreal pole B of a magnet (Fig. 5.), which may be of the horse-shoe form, a piece of soft iron $a\ b$, wholly destitute of magnetic powers, is presented, a similar displacement of the magnetic forces of its elements occurs as in the magnet itself; or $a\ b$ becomes a magnet by induction, and may attract and induce magnetism in a second bar $a'\ b'$; both of which continue magnetic so long as the first remains in the same position, and under the influence of A B. These induced magnets must have the same polarized molecular structure as

the original magnet, but their magnetism is only temporary, and is immediately lost when they are removed from the permanent magnet. The displacement of the magnetisms in these induced magnets commences at the extremity a of $a\ b$, in contact with B, which extremity has the opposite magnetism of B, (the different kinds of magnetism being mutually attractive,) and is the austral pole of $a\ b$; and b is its boreal pole. Of $a'\ b'$, again, the

upper extremity a' , in contact with b' , is the austral, and the lower extremity b' , the boreal pole, or $b b'$ have the same kind of magnetic power as the pole B of the original magnet, from which they are dependent. A third bar of soft iron placed at b' is likewise polarized, and the series of induced magnets may be still farther extended, but the attractive powers developed in the different members of the series, become less and less with their distance from the pole B of the original magnet.

FIG. 6. FIG. 7.



A similar set of bars may be connected with A (Fig. 6.), which become temporary magnets also according to the same law, the lower extremities of this set being austral. On now uniting the lower extremities of both sets by another bar of soft iron $a'' b''$, (Fig. 7.), either set renders $a'' b''$ a magnet, having its austral pole at a'' and its boreal pole at b'' ; and acting together, they communicate a degree of magnetism to the uniting bar, greater than either set possessed before they were united. By this

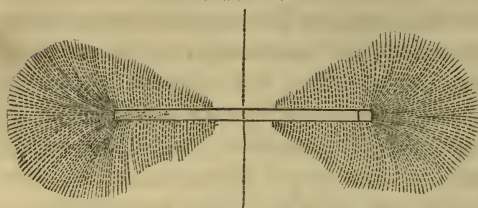
connexion also the inductive actions of each set of bars is brought to bear upon the other, and the attractive forces at all their poles are thereby greatly increased. In the most favourable conditions as to the size and connexion of the temporary magnets, with relation to the primary magnet, the former, however numerous, should each acquire powers equal to those of the original magnet. This general enhancement of power in the induced magnets, has been acquired by completing the circle of them between A and B.

It is also important to observe, with a view to the future application of the remark, that a single bar of soft iron, or *lifter*, as $b a$, (Fig. 8.), connecting the poles of a magnet A B, not only acquires at a and b equal, though opposite

FIG. 8. powers to the contiguous poles of the magnet, but also reacts by induction on these poles themselves, and increases their magnetism. The original magnetic forces of A and B are therefore increased, by the opportunity to act inductively, which the connecting bar affords them. The threads of steel filings which are taken up by a magnet, (see figure 9) illustrate the inductive action of magnetism,



FIG. 9.



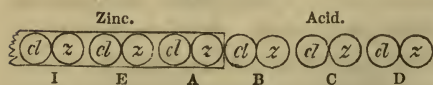
for each grain of steel is a complete magnet. It will be observed also that these threads diverge from each other; because while unlike poles are in

contact in each thread which attract, like poles are in contact of adjoining threads which repel. This repulsion of polar chains by each other, there will be occasion again to recur to.

Chemical polarity and induction.—With these elementary notions of polarity and the mode of action of a force by induction, we may return to the chemical phenomena of the voltaic circle. It is to be assumed that the zinc and hydrochloric acid are both composed of particles, or molecules, which are susceptible of a polarized condition, like the particles of soft iron, in which condition, the opposite ends of each molecule possess different and contrary attractive powers. Of hydrochloric acid, the chemical atom may be taken as the polar molecule, and it will therefore consist of an atom of chlorine and an atom of hydrogen associated together. The polar molecule of zinc may be supposed, for a reason which will afterwards appear, to consist of a pair likewise of associated atoms, which, however, are in this body both of the same element. The powers developed in a polarized molecule of zinc and of hydrochloric acid are the same. One pole of each molecule has the attraction, or affinity, which is characteristic of zinc, or *zincous* attraction, and may be called the zincous pole; while the other has the attraction, or affinity, which is characteristic of chlorine, or *chlorous* attraction, and may be called the chlorous pole. Polarity is not an ordinary condition of the particles of either the zinc or acid, but is developed in both when brought into contact with each other. Such is to be supposed the mode in which chemical affinity always acts.

Zinc and acid in contact may therefore be represented (Fig.

FIG. 10.



10.) by trains of associated pairs of atoms. In the molecule of hydrochloric acid B, which is in contact with

zinc, the chlorous affinity is thereby developed on the side next the zinc, and we have there the constituent chlorine atom forming the chlorous pole, the fluidity of the acid allowing its molecule to take

that position, which may be indicated by inscribing *cl* in the circle which represents the chlorine atom. The other atom of the particle B, or the hydrogen, comes therefore to be the seat of the opposite, or zincous pole, and is marked *z*. Of the two atoms forming the polarizable molecule A of the zinc, the exterior atom which is in contact with the acid has thereby zincous attraction developed in it, and becomes the zincous pole, while the interior becomes the chlorous pole, as indicated in both by the inscribed letters. This polar condition of the zinc and acid particles A and B must be supposed the necessary and immediate consequence of their simple contact.

But each of these particles throws a train of particles of its own kind into a similar state of polarity; A, the contiguous particles E and I of the zinc, and B the contiguous particles C and D of the acid. For *cl* of A becoming a chlorous pole, develops near it an opposite, or zincous poles in *zn* of E, and a chlorous pole in *cl*, the more remote extremity of E; in the same manner as the austral pole of a magnet develops, by induction, a boreal and austral pole in a piece of soft iron applied to it. And as the induced magnet, thus formed, will react upon a second piece of iron, and render it also magnetic, so the polarized particle E, renders I similarly polar. The polarized condition of the particles C and D of the acid is produced by B in the same manner. But as in a series of induced magnets (Fig. 5.), the magnetism acquired diminishes with the distance from the pole of the original magnet, so in trains of chemically polarized molecules, such as A, E, I and B, C, D, the amount of polarity developed in each molecule will diminish with the distance from the sources of induction A and B; I being polarized to a less degree than E, and D than C.

In the electrical theory of the voltaic circle as modified by Mr. Faraday, the zinc and hydrochloric acid are equally supposed to have a polarizable molecule. The polarity is also developed in these molecules by their approximation or contact. The molecule of hydrochloric acid is supposed to contain the positive and negative electricities which possess contrary powers, like the two magnetisms; and are in combination and neutralize each other, in the non-polar condition of the molecule. But the contact of zinc causes the separation of the two electricities in the acid molecule, its atom of chlorine next the zinc becoming negative, and its atom of hydrogen

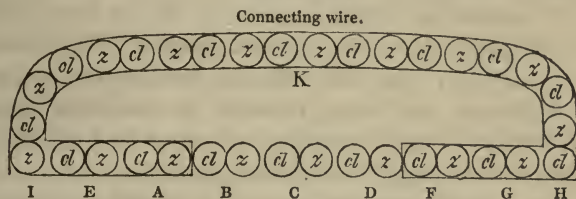
positive. The electricities of the zinc molecule are separated at the same time, the side of the molecule next the acid becoming positive, and the distant side negative. The positive and negative sides of the two different molecules are thus in contact, the different electricities, like the different magnetisms, attracting each other. Hence, one side of each molecule is said to be positive instead of zincous, and the other side to be negative instead of chlorous. Polarity of the molecule is supposed in both views, but on one view the polar forces are the two electricities, on the other two chemical affinities. The difference between the two views is little more than nominal, for in both the same powers and properties are ascribed to the acting forces. The electricities are supposed to be the cause of the chemical affinities, but it may with equal justice be assumed that chemical affinities are the cause of the phenomena reputed electrical. One set of forces only is necessary for the explanation of the whole phenomena of combination, and the question is, whether are these forces electrical or chemical? Shall electricity supersede chemical affinity, or chemical affinity supersede electricity? If the electricities should be retained in discussing the voltaic circle, their names might be changed with some advantage, the positive be called zincous electricity, and the negative, chlorous electricity, which express (as will appear more clearly afterwards), the nature of the chemical affinities with which these electricities are invested, and of which they are indeed constituted the sole depositaries. The propagation of the effects to a distance is supposed to take place by the polarization of chains of molecules, on the electrical as well as chemical theory of the voltaic circle, so that the explanations which follow, although expressed in the language of the chemical theory, are the same in substance as those which are given on the electrical theory as at present understood.

If the attractions of the respective zincous and chlorous poles of A and B which are in contact, rise to a certain point, the atom *z* of A is detached from the mass of metal and combines with the atom *cl* of B, which last atom is disengaged at the same time from its hydrogen. Chloride of zinc is produced and dissolves in the acid liquid, while hydrogen is disengaged and rises from the surface of the metal; or we have the ordinary circumstances of the solution of an isolated mass of zinc in hydrochloric acid.

SIMPLE VOLTAIC CIRCLE.

When the zinc is pure, or its surface amalgamated with mercury, the zincous and chlorous attractions of the touching poles of A and B are not sufficiently intense to produce these effects, and combination does not occur. Let a copper plate

FIG. 11.



F G H (Fig. 11.), be then introduced into the acid, and connected by a metallic wire H K I with the zinc. The particles of the acid assume chlorous and zincous poles as before, so also do those of the zinc, and the chain of polarized molecules is now continued through the zinc and wire to the copper, the exterior particle F of which, it will be observed, comes thereby to present a chlorous pole to the acid. The contiguous particle D of acid is thus exposed to a second induction from the chlorous polarity of the copper, which increases the zincous polarity of the side of D next F, and, therefore, cooperates in enhancing the polarized conditions already assumed by the chain of acid particles extending between the two metals. An endless chain or circle of polarized molecules symmetrically arranged is thus formed, such as exists in a magnet of which the poles are united by a lifter, in which every particle in the chain has its own polar condition elevated by induction, and at the same time does itself react upon and elevate the polar condition of every other particle in the chain. The result of this is that the primary attraction of the zinc atom *z* of A, for the chlorine, *cl* of the hydrochloric acid B is increased, and attains that degree of intensity at which the resistance to the impending combination is overcome, and the *z* and *cl* of A and B unite. But in a circle of polar molecules, in which the condition of any one molecule determines and is determined by that of every other, the intensity of the polar condition is necessarily the same in every element of the circle. The chemical polarity, therefore,

of the other particles forming the chain must increase to an equal degree with A and B, when the circle is completed, and the same change must now occur in all of them that has occurred in A and B. The pole of B next C is intensely zincous, while that of C next B is intensely chlorous, whence the chlorine and hydrogen *cl* and *z* of these two particles combine together. At the same time, and for the same reason, the hydrogen *z* of C unites with the chlorine *cl* of D; and so on, through a chain of particles of hydrochloric acid of any length, till the copper is reached, when the last acid particle, D in the figure, yields its hydrogen *z* to the chlorous pole of the copper *cl*. But *the hydrogen*, not being capable of combining with the copper, *is liberated as gas upon the surface of that metal*.

Some internal change of a similar character appears to take place in the chain of polarized molecules extending through the metals themselves—a series of molecular detachments and re-attachments, among the atoms of their polar molecules, like the decompositions and recompositions in the acid, causing evolution of heat and other phenomena, generally reputed electrical, which the zinc and copper plates and the connecting wire exhibit.

The polar molecule of the metals has been assumed to contain two atoms (like that of the acid), with the view of assimilating these intestinal changes in the solid to those occurring in the fluid portion of the voltaic circuit, and also because it appears to account for the advantage of amalgamating the zinc surface. In the amalgamated plate, it is not zinc itself, but a chemical combination of mercury and zinc which is presented to the acid, in which mercury is the “negative” element, and which might, therefore, be called a hydrarguret of zinc. That combination likewise is *fluid*. It must constitute the polar molecule, which will then consist of an atom of mercury as chlorous pole, and an atom of zinc as zincous pole, and not of two atoms of zinc. These metallic molecules are also capable of movement from their fluidity, and will, therefore, place themselves in forming a polar chain with their unlike poles together, as the fluid acid particles arrange themselves. So that in an amalgam of zinc, of which A, E and I are polar molecules (Fig. 8.), all the atoms marked *cl* are mercury, and those marked *z* are zinc. It thus follows that, when by contact with an acid the amalgam is polarized, it presents a

face of zinc only to the acid. If the mercury were exposed to the acid, that metal would completely derange the result, acting locally like a copper plate, as will afterwards be explained. The previous combination of the zinc (with mercury,) likewise prevents that metal from yielding easily to the chlorine of hydrochloric acid; and the zinc of the amalgam is, therefore, not dissolved, till the affinities are enhanced by the introduction of a copper plate into the acid, and the formation of a voltaic circle.

It would thus appear that zinc, associated with copper, dissolves more readily in the acid than when alone, because the attraction or affinity of the zinc, for chlorine is increased by the completion of a circle of similarly polarized particles, in the same manner as the magnetic intensity at one of the poles of a magnet is increased on completing the circle of similarly polarized molecules, by connecting that pole by means of soft iron with the other pole (Fig. 6., page 203).

Although the terms of the electrical hypothesis are at present avoided, still it will be convenient to denominate the zinc, being the metal which dissolves in the acid, the active or *positive* metal, and the copper, which does not dissolve, the inactive or *negative* metal of the voltaic circle.

Looking to the condition of the two connected metals in the acid, it will be observed that the surface of the zinc presented to the acid has zincous affinity, or is zinco-polar, but the surface of the copper presented to the acid has, on the contrary, chlorous affinity, or is chloro-polar. Such a condition of the copper is necessary to the propagation of the induction; and the advantage of copper or platinum as the negative metal in a voltaic arrangement depends upon there being little or no impediment to either of these metals assuming the chlorous condition, that can arise from the peculiar affinity of the metals named for the chlorine of the acid; an affinity which tends to cause them to be superficially zincous instead of chlorous. If the second metal were zinc, the surface of it would be disposed to dissolve in the acid, and becoming on that account zincous, would induce a polarization in the intermediate acid, in an opposite sense, from that induced by the first plate of zinc; which counter polarizing actions would mutually neutralize each other. The acid between the two zinc plates would

be like a piece of iron connecting two like magnetic poles, which itself is not then polarized.

But if one of the two zinc plates were less disposed to dissolve in the acid than the other, from the physical condition of its surface, from the acid being weaker there, or from any other cause, then the plate so situated might become negative to the other, and a voltaic circle of weak power be established, in which both metals were zinc.

If zinc is alone in the acid, and every superficial particle of the metal equally disposed dissolve, then the zinc everywhere exposes a surface in a state of zincous polarity; and an inductive circle in the liquid, starting from one particle of the zinc and returning upon another, cannot be established, as this requires that a part of the zinc surface be chlorous. But if the

FIG. 12.



zinc contains on its surface a single particle of copper, F (Fig. 12.), a chlorous pole is created upon which an inductive circle starting from an adjoining particle of zinc, A, and passing through the liquid, may return as shewn in the figure. It is the formation of such circles that causes impure zinc, which is contaminated by other metals, to dissolve so much more quickly in an acid than the pure metal. Why such circles are not formed when the positive metal in combination with the zinc is mercury, which forms a fluid alloy, has already been accounted for; and the nature of the evil which might otherwise attend the amalgamation of the zinc is now evident.

The whole chain polarized molecules in the voltaic circle admits of a natural division into two segments, the acid or liquid segment, B C D (Fig. 10.), and the metallic segment, A K F, each of which has a pair of poles, the unlike poles of the two segments being opposed to each other. The pole at B of the acid portion is chlorous, and is opposed to the zincous pole at A of the metallic segment; while the pole of the liquid segment at D is zincous, and is opposed to the chlorous pole of the metallic segment at F. The distribution of polarity in these two segments is, therefore, the same as in two magnets with their unlike or attracting poles in contact.

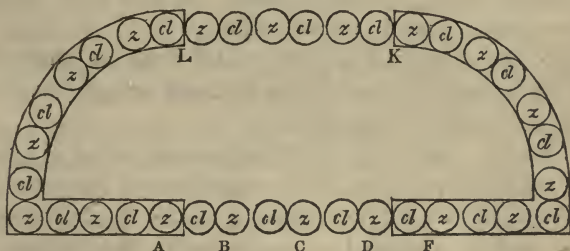
Such, then, is the action of affinity by induction, which the mere introduction of zinc and copper in contact into the same

acid liquid, is sufficient to develop, and which accounts for the discharge of the hydrogen upon the surface of the copper in such an arrangement, the remarkable phenomenon by a description of which this subject was introduced.

It remains for us to apply the same principles to explain the additional phenomena of the second case described, in which the connecting wire, supposed to be of platinum, between the zinc and copper plates, is divided, and the broken extremities introduced into hydriodic acid (Fig. 3, page 199.)

Broken at any point, as at K, (Fig. 12.), it is evident that if the polarized condition be still sustained, the portion of the metallic segment connected with the copper plate will terminate with a zincous pole at K, and that connected with the zinc, with a chlorous pole; which may be indicated respectively

FIG. 13.

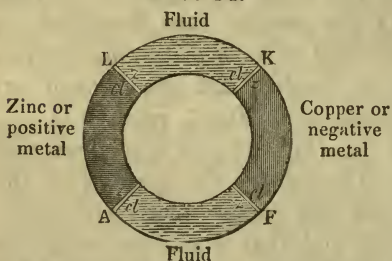


by K and L in Fig. 13. When hydriodic acid is interposed between K and L, the breach is repaired by the polarization of a chain of particles of that acid. The extremity K, being zincous induces chlorous polarity in the side of the hydriodic acid particle which it touches, in consequence of which the iodine atom (the analogue of chlorine) of the hydriodic acid molecule is presented to that pole, and liberated there when decomposition occurs. The extremity L of the zinc or positive metal element is chlorous, and therefore induces zincous polarity in the particle of hydriodic acid which it touches, and hydrogen (the analogue of zinc) is liberated there. The polarity in an induced circle must necessarily be of equal intensity at every point in it, and being sufficient at A to cause the decomposition of the hydrochloric acid, must also decompose the hydriodic acid between K and L, otherwise it is never established at A, nor any where else.

In the present arrangement, the voltaic circle is broken into

four segments, or has four polarized elements, every terminal pole of which is in contact with a pole of a different name; and the whole arrangement may be compared to a circle of four magnets with the attractive poles in contact.

FIG. 14.



These elements are: —
First, the zinc plate or positive metal, A L, of which the end at A, in the hydrochloric acid (Fig. 14.), has zincous affinity, and the end at L, in the hydriodic acid, chlorous affinity.

Secondly, the body of hydrochloric acid, A F, between the zinc and copper plates, of which the surface at A, in contact with the positive metal, has chlorous, and that at F in contact with the negative metal, zincous affinity.

Thirdly, the copper or negative metal F K, of which the end at F in the hydrochloric acid, has chlorous affinity, and at K, in the hydriodic acid, zincous affinity.

And fourthly, the body of hydriodic acid, K L, between the zincous and chlorous poles of the negative and positive metals, of which the surface K, in contact with the negative metal, is chlorous, and the surface L, in contact with the positive metal, zincous.

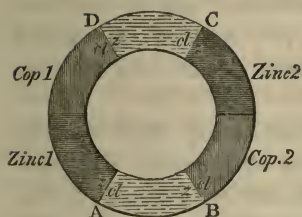
In every voltaic circle employed to produce decomposition, these four elements are to be looked for. Hereafter, in adverting to any one of these elements it will be sufficient to confine our notice to its terminal polarities or affinities, without recurring to the polarized condition of the element itself, upon which its terminal affinities depend.

COMPOUND VOLTAIC CIRCLE.

In both the arrangements described there is only one source of polarizing force, namely the action between the zinc and acid at A. But a circle of a similar nature may be constructed embracing within itself two or more of such primary sources of polarizing power, and the intensity of the polar condition of the whole circle be thereby greatly increased.

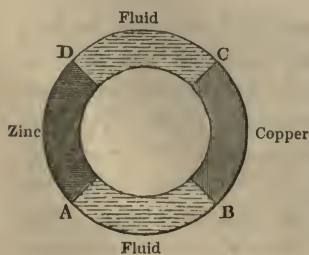
Figure 15 represents such a circle in which there are two

FIG. 15.



zinc plates, both supposed to be in contact with hydrochloric acid, namely at A and at C, and a copper plate attached to each of these zincs. The circle is made up of two pairs of copper and zinc, copper and zinc, with acid between each pair. The polar condition of such a circle will easily be observed. By the contact of the acid and zinc at A, a zincous pole is established there in the first zinc plate, and a chlorous pole in the acid, which are so inscribed in the diagram. These occasion the formation of a chlorous pole at D in the first copper, the united zinc and copper A D forming together one polar element; and a zincous pole at B in the acid, the column A B of acid, being the second polar element. The further effect of the induction is to produce a chlorous pole at B in the second copper, of which the corresponding zincous pole is at C, in the second zinc; the united zinc and copper B C forming together a third polar element. And, as a last consequence of the inducing force originating at A the column of acid between C and D becomes a fourth polar element of the circle, having a chlorous pole at C and a zincous pole at D. Now it will be observed that the chemical affinity between the acid and zinc at C tends to produce the same polar conditions at that point, as are already established there from the effect of induction. The extremity of the zinc plate at C is in fact zincous both primarily and by induction; and the acid in contact with it, likewise chlorous, both primarily and by induction; and generally throughout the whole circle, the polar conditions determined by the second chemical action at C are the same as those determined by the first action at A.

FIG. 16.



In the last arrangement, the inductive actions are in the same direction, and favour each other; but a circle may be constructed in which the inductions, being in opposite directions, oppose and neutralize each other. Thus if A D (Fig. 16.) be entirely zinc, both its extremities being exposed to acid, will tend

equally to be zincous. In the same way if B C be entirely copper, the condition of both its extremities will be chlorous from the action of the acid on the two ends of the zinc; and consequently the elements of such a circle could have no polarity.

A circle is represented in Fig. 17, containing three sources of polarizing force. It consists of three alternations of copper

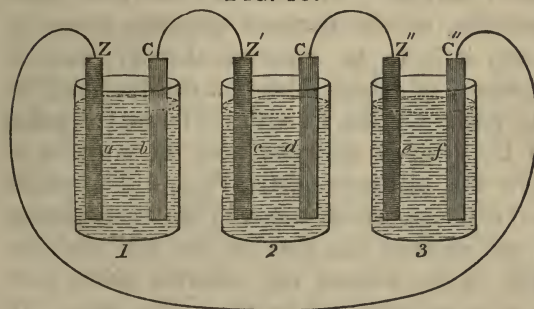


and zinc symmetrically arranged, and forming three polar elements F A, B C and D E, with three acid columns between these alternations, which form three additional polar elements, A B, C D and E F. The number of alternations of copper and zinc, with acid, may obviously be increased to any extent, and the chemical action of the acid on the zinc in each alternation is found to increase in a marked manner up to the number of 10 or 12 alternations. This increase of the affinity is undoubtedly owing to the favouring inductive action, which the chemical actions at the different points have upon each other. Such a compound circle may be compared to a number of magnets disposed in a circle with their attracting poles together, of which each would have its magnetic intensity exalted by induction from all the rest. When such a circle is broken at any point, all chemical action and polarization cease till contact is again made, and the circuit completed. The polarization, too, being the result of a circular induction involving so many lines or chains of particles, cannot, when once established, be more nor less at any one point in the circuit than at others. The resulting chemical action must therefore be every where equal in the circle, and consequently the same quantity of zinc be dissolved and hydrogen evolved in each acid.

If any metallic element of this compound circle be broken, and a polarizable liquid be interposed between the metallic extremities so as to complete the circuit, decomposition occurs in that liquid as in the simple interrupted circle (Fig. 12.) The polarizing influence of the compound circle being of high intensity, more numerous and difficult decompositions are effected by means of it, than by the simple circle. The compound voltaic circle is indeed a decomposing instrument of great efficiency.

If in this arrangement the position of one of the metals in the series be reversed, so that a zinc is where a copper should be, then by the action of the acid on that zinc polarization in the wrong direction is occasioned, which greatly diminishes the general polarity of the circle, reducing it in an arrangement of ten alternations to one fourth according to Mr. Daniell.

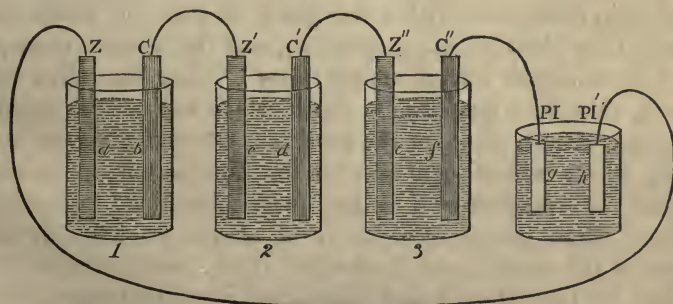
In the first of the two annexed diagrams (Fig. 18.) is represented a compound circle, such as is employed to produce decomposition and called a voltaic battery, consisting of three acid jars, each of which contains a zinc and copper plate; and



which are termed active cells, as they are sources of polarizing power, from the action of acid upon zinc which takes place in them.

In the second diagram (Figure 19), the same arrangement

is repeated with the addition of a third jar, termed the decomposing cell, which contains any polarizable liquid, with two platinum plates immersed in it. Each copper, it will be seen, is connected by a wire with the following zinc, and in the first diagram, the copper in the third cell C'' is immediately connected with the zinc in the first cell Z by a wire, and the circuit thus completed. The polar elements in the



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circle of the first diagram, it will be found are six in number; namely, the three acid columns between the metals in the cells, *ab*, *cd* and *ef*; and the three pairs of zinc and copper plates, each of which forms a single polar element, of which the surface of the zinc is the zincous, and the surface of the copper, the chlorous pole. In the second diagram, one of these metallic elements *Z C''* is divided, and a polarizable liquid *gh*, in the cell of decomposition, interposed between the broken extremities *Pl* and *Pl'*. To ascertain the polar condition of the extremities, or the terminal platinum plates in the decomposing cell, it is to be observed that *Pl'* with *Z* forms one polar element, of which *Z* being a zincous pole, *Pl'* must be a chlorous pole. Again, *Pl* with *C''* forms one polar element, of which *C''* being a chlorous pole, *Pl* must be a zincous pole. Now the platinum plates *Pl* and *Pl'* which are thus zincous and chlorous, are disposed in the decomposing cell, in regard to one another, the first to the left, and the second to the right, as the zincous and chlorous plates, (the zinc and copper), also are arranged in the active cells. It will be convenient to distinguish, by names, the poles which these terminal platinum plates constitute, as they are much more frequently referred to, and of greater consequence than any other poles in voltaic battery, when used as an instrument of decomposition as it constantly is. The chlorous plate *Pl'* which is in connexion with a zinc plate *Z*, may be called the *chloroid* (like chlorine, quasi-chlorine), and the zincous-plate *Pl* which is connected with a copper plate *C''* may be called the *zincoid*, (like zinc, quasi-zinc), names which express the virtual properties of each plate, or the particular attractive power and affinity which each of them acquires from its place in the circle.

When hydrochloric acid is the polarizable liquid interposed between these plates, chlorine is of course attracted by the surface of the zincoid and discharged there, and hydrogen by the face of the chloroid and discharged upon that plate. On the electrical hypothesis, the same plates are variously denominated:

The *zincoid* as the positive pole, the positive electrode, the anode, and the zincode.

The *chloroid* as the negative pole, the negative electrode, the cathode and the platinode.

The cell of decomposition thus interpolated in the voltaic

circle is an obstacle to induction, and reacts on the whole series, reducing the chemical action and evolution of hydrogen in each of the active cells by at least one third. In that retarding cell itself, the amount of decomposition, is necessarily the same as in the other cells. Mr. Daniell found the chemical action reduced to one tenth, in a series of eight active and two such retarding cells; and entirely stopped by three retarding to seven active cells.

OF THE SOLID ELEMENTS OF THE VOLTAIC CIRCLE.

The elements of a voltaic circle are obviously of two different kinds, the metals or solid portions, through the substance of which chemical induction is propagated without decomposition, and the liquids in the cells, which yield to the induction and suffer decomposition. In reference to the first, it is to be observed that, as only iron and one or two other metals of the same natural family are susceptible of magnetic polarity, so the susceptibility of chemical polarity which appears in the voltaic battery is not possessed by solids in general, but is confined to the class of bodies to which zinc belongs,—the metals, all of which possess it, with the addition of carbon in the form of charcoal, and the sulphuret of silver when heated. The non-metallic elements with their compounds, and the oxides, sulphurets and other compounds of the metals, some of which exhibit the metallic lustre, are all destitute of this power, and cannot, therefore, be used as solid elements of the circle. A body available for this purpose is termed a *conductor* on the electrical hypothesis, a name which may be retained as it is not at variance with the function assigned to the metals in the circle viewed as a chemico-polar arrangement. Two different metals are combined in a circle, one of which is acted on by the liquid, and, therefore, called the active or the positive metal, while the other is not acted upon, and is, therefore, called the inactive or the negative metal; and it has already been stated that the more easily acted on by the liquid or the more highly positive the one metal, and the less easily acted upon, or more negative the other metal, the more proper and efficacious is the combination. In the following table several of the metals are arranged in the order in which they appear positive or negative to each other, when acted on by

the acid fluids commonly employed in the voltaic battery. Each metal is positive to any one below it in the table, and negative to any one above it.

Most positive.

Potassium.
Sodium.
Manganese.
Zinc.
Cadmium.
Iron.
Nickel.
Cobalt.
Lead.
Tin.
Bismuth.
Copper.
Silver.
Mercury.
Palladium.
Platinum.
Rhodium.
Iridium.
Gold.

Most negative.

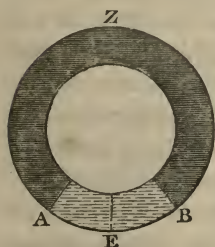
Zinc which stands high in the list, is the only metal which can be used with advantage in the voltaic battery, as the positive metal. Although closely approaching zinc in the strength of its affinities, iron is ill adapted for the purpose, from the impossibility of amalgamating its surface, the irregularity of its structure, and certain peculiarities of this metal in reference to chemico-polarity. Platinum forms an excellent negative metal from the weakness of its affinities, and is generally used for the plates in the cell of decomposition. Silver also is highly negative, but copper is the only negative metal, which from its cheapness can be used in the construction of active cells of ordinary magnitude.

But although the difference between two metals in point of affinity be very small, yet their association in the same acid always gives a decided predominance to the affinity of the more positive, by causing the surface of the other to become chlorous,

and therefore wholly inactive in an acid fluid. A negative metal may thus be protected from the solvent action of saline and acid liquids, by association with a more positive metal; iron, for instance, by zinc, as in articles of *galvanized iron*, which are coated with the former metal; and copper by either zinc or iron, as was remarkably illustrated in the attempt made by Sir H. Davy to defend the copper sheathing of ships from corrosion in sea-water, by means of his *protectors*. These were small masses of iron or zinc fixed upon the ship's copper, at different points under the water line. They completely answered the purpose of protecting the copper, but unfortunately gave rise to a deposition of earthy matter upon that metal to which barnacles and sea-weeds attached themselves, and thereby diminished the facility of the ship's motion through the water.

A weak galvanic circle may even be formed of a single positive metal in an acid, as the zinc A B (Fig. 20), provided the

FIG. 20.

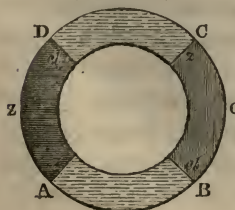


surfaces of the metal exposed to the acid at A and B are in different conditions as to purity or mechanical structure, and therefore unequally acted upon by the acid; whereupon the part least disposed to dissolve becomes negative to the other. A zinc plate may also be unequally acted on and thrown into a polar state, from the liquid in which it is immersed varying in composition and activity, at different points of the metallic surface.

A circle may thus be formed of one metal A B with two liquids A E and E B, which merge into each other, and form together one polar element A B.

The two metals in a circle have generally been exhibited in metallic contact, and forming together one polar element, but they may be separated, as are the zinc and copper plates A D and C B in the diagram (Fig. 21), by two polarizable fluids,

FIG. 21.



provided these fluids are such as a strong acid at A B, and as iodide of potassium at D C, the first of which acts very powerfully on zinc, while the other acts very feebly upon that metal (unless associated with copper); so that of the consequent opposing inductions, that originating at A greatly exceeds and overpowers that from D.

It is likewise necessary that the fluid D C be of easy decomposition, so as to yield to the polarizing power of the single circle. In this arrangement, however, it is obvious that the zinc itself forms a complete polar element, of which A is the zincous, and D the chlorous pole; and the copper also an entire polar element of which B is the chlorous, and C the zincous pole.

The preceding table exhibits the relation which the metals enumerated assume to each other, in the acid and saline solutions usually employed as exciting fluids. But the relation of any one metal to another is not the same in all exciting fluids. Thus when tin and copper are placed in acid solutions, the former is most rapidly corroded and becomes the positive metal, according to its position in the series, but if they are put into a solution of ammonia which acts most upon the copper, then the latter becomes the positive metal. Copper is positive to lead in strong nitric acid, which oxidizes the former most freely, whereas in dilute nitric acid, by which the lead is most rapidly dissolved, the lead is positive.

LIQUID ELEMENTS OF THE VOLTAIC CIRCLE.

With the view of simplifying the statement of the chemical changes which occur in the voltaic circle, the exciting fluid has hitherto always been supposed to be hydrochloric acid (chloride of hydrogen), and this compound is a fair type of the class of bodies which are available for the purpose of bringing these changes into play. The exciting fluid is always a *saline body* in the general sense, that is, a compound of a salt-radical, such as chlorine, with a basyle, such as hydrogen or a metal. The chloride of copper, chloride of sodium, chloride of ammonium, or the chloride of any other basyle may be substituted for hydrochloric acid, although not all with the same advantage; and the chlorides of basyles may be replaced by their iodides, sulphatoides (sulphates), nitratoides (nitrates) and salts of other acids, as exciting fluids, provided they have the condition of liquidity, which gives mobility to their particles and permits that disposition of them which is assumed in a polar chain. The liquids, which yield in the cell of decomposition, are of the same nature, although the liquid which forms the best exciting fluid is not always the most easily decomposed in the decomposing cell.

The positive metal which is exposed to the exciting fluid always acts in one way, displacing the basyle and combining with the salt-radical of that body; in the manner the zinc has been seen to liberate hydrogen and combine with chlorine, when hydrochloric acid is the exciting fluid. The positive metal is thus substituted for a similar basyle in a pre-existing saline compound. That metal may dissolve in another manner, by uniting directly, for instance, with free chlorine or iodine in solution, but then no polarization follows. A chain of particles of chlorine may extend from the zinc to the associated negative metal, but they are not polarized, as a chain of hydrochloric acid particles would be in the same circumstances. The particles of these free elements appear to be incapable of that polar condition, having chlorous affinity on one side and zincous on the other, of which both the solid and liquid constituents of the voltaic circle must be susceptible. Judging from the uniformity in composition of exciting liquids, their susceptibility of polarization depends on their consisting of an atom of basyle and an atom of salt-radical, which may become respectively the locus of zincous and chlorous polarity. Or as chlorine belongs to the salt-radicals and zinc to the basyles, and each may be taken to represent its class, the exciting bodies may be said to be capable of having a chlorous and zincous pole, because they consist of a chlorous and zincous element. Such particles may be looked upon as in a state of tension when forming a part of a polar chain, each about to divide into its chlorous and zincous atoms. Mr. Faraday has established that all exciting liquids are binary compounds of single equivalents of salt-radical and basyle, or *proto-compounds*, such as hydrochloric acid itself, proto-chloride of tin, &c. Other saline bodies which are *per-compounds*, such as bichloride of tin, are not exciting or polarizable, because, as it may be supposed, they are not naturally resolvable into a chlorous and zincous atom, but into a chlorous atom and *another salt*; the bichloride of tin, for instance into chlorine and proto-chloride of tin. For such saline bodies may all be *ternary* compounds and consist of a binary compound united with an additional quantity of salt-radical. Certain protocompounds, also, which are deficient in the saline character, are not polarizable, such as chloride of sulphur, protochloride of phosphorus and protochloride of carbon. These bodies do not contain a proper basyle.

The zinc or positive metal, too, always forms a proto-compound in dissolving, which is a saline body. The order of the chemical changes in the exciting fluid therefore is as follows : The zinc in decomposing a binary compound and forming a binary compound, liberates an atom of its own class; which atom repeats the same actions; supplying at the same time another atom of the same kind to act in the same manner, and that another, from the zinc to the copper plate. The combining bodies are always a basyle and a salt-radical, and therefore only two kinds of attraction or affinity are at work throughout the chain, those of a basyle and a salt-radical, the zincous and chlorous affinities. Hence, in the present subject of chemical polarity, we have to deal with but two attractive forces, the zincous and the chlorous, as in magnetism with but two magnetic forces, the austral and the boreal.

On the electrical hypothesis a body which is thus decomposed in the active cells, or in the cell of decomposition, is called an *electrolyte* (decomposable by electricity), and this kind of decomposition is distinguished as *electrolysis*. The chemical expressions equivalent to these are *zincolyte* and *zincolysis*, the decompositions throughout the circle being referred to the inductive action of the affinities of zinc or the positive metal.

The characters of the two constituents of a zincolyte may be shortly noticed. The class of basyle constituents is composed of the metals in their order as positive metals, beginning with potassium and terminating with mercury, platinum and the less oxidable metals. Ammonium has a claim to be introduced high in this list, and should probably be accompanied by the analogous basyles of the vegeto-alkalies, although in respect to the decomposition of their salts in the voltaic circle, we have no precise information. Hydrogen likewise finds a place near copper in this class.

At the head of the salt-radical constituents of zincolytes may be placed iodine and the other members of the chlorine family. These are followed by the salt-radicals of the sulphates, nitrates, carbonates, acetates, and other oxygen-acid salts. Sulphur must be allowed to follow the last as the salt-radical of the soluble sulphurets, and the lowest place be assigned to oxygen, as the salt-radical of the soluble metallic oxides, of oxide of potassium, for instance, and of water. It is unusual to speak of oxygen as a salt-radical, and of caustic potash and water as salts, but the

binary theory of salts recognizes no essential difference between the chloride, sulphatoxide, and oxide of a basyle, the oxide being connected with the more highly saline compounds through the sulphuret, and the chain of salt-radicals from iodine to oxygen being continuous and unbroken.

The facility of decomposition of different zincolytes appears to depend more upon the high place of their salt-radical than upon the nature of their other constituent. The iodides, for instance, as iodide of potassium and hydriodic acid, are the most easily decomposed of all salts, yielding to the polar influence of the single circle. Then follow the chlorides,—chloride of lead, fused by heat, yielding to a very moderate power. After these the salts of strong oxygen acids, such as sulphates and nitrates either of strong bases, such as potash and soda, or of weak bases, such as oxide of copper and water (the hydrated acids are such salts). The carbonates and acetates, which have much weaker salt-radicals, are still less easily decomposed, and finally oxides are decomposed with great difficulty. Water itself is polarized with such extreme difficulty, and decomposed when alone to so minute a degree, even by a powerful battery, as to leave its claim to be considered a zincolyte when in a state of purity by no means certain.

Widely as the more characteristic salt-radicals and basyles differ, still the classes pass by imperceptible gradations into each other, and form portions of one great circle. Mercury and the more negative metals, although clearly basyles, appear at times to assume the salt-radical relation to the highly positive metals; such a character is evinced in mercury, by the energy with which it unites with sodium and potassium, and by its function in the amalgamated zinc plate of the voltaic circle. So that the salt-radical or basyle character of a body is not absolute, but always relative to certain other bodies.

The addition of a salt or acid, even in minute quantity, to water in the cell of decomposition, causes the copious evolution of oxygen and hydrogen gases at the zincoid and chloroid, and is therefore often spoken of as facilitating, by its presence, the decomposition of the water, in some way which cannot be explained. But the phenomena are unattended with difficulty on the binary theory of saline bodies. When sulphate of soda exists in the water of the decomposing cell, it is sulphatoxide of sodium which is decomposed, SO_4 , the sulphate radical being

evolved at the zincoïd and sodium at the chloroid. But the sodium having a strong affinity for oxygen reacts upon the water at the pole, forming soda and liberating hydrogen, which therefore appear together; while SO_4 having, as a high salt-radical, a powerful affinity for hydrogen, likewise decomposes water, and thus evolves oxygen, which, with a free acid, appears at the zincoïd. A solution of chloride of sodium is decomposed in the same manner, its elements chlorine and sodium being attracted to the zincoïd and chloroid respectively, but neither of these elements appearing as such. Both decompose water and thus produce oxygen with hydrochloric acid at the zincoïd, and soda with hydrogen at the chloroid. It has indeed been ascertained that the polar influence which apparently effects two decompositions in these circumstances, namely, that of water into oxygen and hydrogen, and of a salt into its acid and alkali, is no more in quantity than is necessary to decompose one of these bodies, the circulating power being measured by the quantity of fused chloride of lead decomposed in another part of the circuit (Daniell). There can be little doubt then that only one binary compound is immediately decomposed, and that the two sets of products which appear at the poles, are the results of secondary decomposition. Indeed the decomposition of salts in the voltaic circle affords considerable support to the binary theory of these bodies (page 164).

Secondary decompositions.—The products of voltaic action are frequently of that secondary character, the original products being lost from their reaction upon the liquid in which they are produced, or upon the substance of the metallic poles. Thus salts of the vegetable acids often afford carbonic acid, and salts of ammonia nitrogen, instead of oxygen, at the zincoïd; the oxygen liberated having reacted upon the combustible constituents of these bodies. Nitrates, again, may afford nitrogen, or nitric oxide, at the chloroid, in consequence of the oxidation of the hydrogen evolved there. The nascent condition of the liberated elements favours such secondary actions. When the zincoïd is composed of a positive metal, such as zinc itself or copper, the chlorous element is absorbed there, combining with the metal. The decomposition of a salt is also then much easier, the action of the circle being greatly assisted by the proper affinity of the matter of the zincoïd for a chlorous body. Insoluble sulphurets, chlorides and other compounds of a posi-

tive metal acting as the zincoid, have thus been slowly produced, in a single circle with a weak exciting fluid; which products have exhibited distinct crystalline forms, resembling natural minerals, not otherwise producible by art. The hydrogen evolved upon a platinum chloroid, immersed in the solution of a copper or iron salt, may also reduce these metals upon the surface of the platinum, in the form of brilliant octahedral crystals. In the active cells themselves a secondary decomposition is apt to occur, the hydrogen evolved decomposing the salt of zinc which accumulates in the liquid, and occasioning a deposition of that metal upon the copper plate; an occurrence which may determine an opposite polarity, and cause the action of the circle to decline. But on disconnecting the zinc and copper plates, the foreign deposit upon the latter is quickly dissolved off by the acid. The inconvenience of this secondary decomposition in the exciting cells is avoided by dividing the cell into two compartments, by a porous plate of earthenware, or by a humid membrane, interposed between the zinc and copper plates. The salt of zinc formed about that metal is prevented from diffusing to the copper, by the diaphragm, although it allows, from its porosity, a continuity of liquid polarizable particles between the metals.

Before leaving the subject of the liquid and solid elements of the voltaic circle, I may offer for consideration some opinions respecting their internal constitution, of a more speculative character, which the chemical theory of the voltaic circle suggests.

The phenomena of electricity of friction, and of high tension appear to indicate that all compound bodies whatever are polarizable, under an intense induction. On the chemical theory this would imply that they are all binary compounds, or at least capable of a binary disposition of their elements. And it is remarkable that recent discovery has detected such a constitution in several bodies containing a large number of atoms, and has rendered it probable in a great many others; ether, for instance, has been found to be the oxide of ethyl, benzoic acid the oxide of benzoyl, and all the essential oils appear to be bodies of a similar constitution. But the molecular constitution of such complex compounds appears not to be fixed and invariable. Alcohol for instance, when free may be the hydrate of ether, that is a ternary compound; but alcohol replaces water

in some salts, and then appears as a binary compound, or the oxide of a new basyle, which is ethyl plus an atom of water. It is not improbable then that under the influence of a powerful induction, compounds may admit of different dispositions of their molecules; that the strong chlorous affinity [of a contiguous polar molecule may develop near it a zincous element, in the most complicated substance.

It comes to be a most interesting subject of inquiry, which I trust is not beyond our reach, what relation have the atoms of a metallic element of the circle to each other, when not in a polar condition? The relation I imagine to be that of combination. Their atoms assume so readily the binary or saline arrangement under induction, that they may be supposed already to possess it. Their atoms may be associated in a congeries, forming a highly complex molecule, the *prototype* of a saline body, in which not only the salt-radical and basyle have their representative atoms of metal, but even the elements of constitutional water, and of water of crystallization. Numerous and most interesting inquiries are suggested by the possible existence of such a molecular structure of the metal. As salts differ from each other in the number and disposition of these accompanying bodies, a sulphate of zinc in its water of crystallization, for instance, from a chloride of the same metal, so one metal may differ from another in the arrangement which it affects, or *salt it resembles*. The molecular arrangement in a metal may even change with its temperature; such arrangements, and the changes they undergo, occasioning a variable inductive action of dissimilar metals in contact upon each other's molecules, and giving rise, in particular, to the phenomena of thermo-electricity.

But the facility with which the polar condition of the molecules of a metal may be reversed, with a change in the direction in the induction affecting it, forbids us to suppose that any particular molecular arrangement of a metal is constant. The metal zinc may have one arrangement which it affects when under no foreign influence, (an arrangement, it may be, impressed upon that metal in its reduction from the ore, by the chemical agencies then at work), but under the influence of different exciting fluids, it must assume different arrangements, analogous to those of the exciting fluid, at one time representing a chloride of zinc, and at another time a sulphate, or reflecting the molecular con-

stitution of the exciting fluid, whatever that may be. To avoid complication, attention has hitherto been confined to the action of the primary affinity of the exciting acid (that of its salt-radical) upon the zinc, but the secondary affinities of the accessory constituents of the exciting acid must also be supposed to act upon the positive metal, although in a subsidiary manner to the primary affinity.

In the constitution of many compound bodies, a provision for the formation of new compounds is observed, similar to what is now supposed to exist in the zinc. In the crystallized sulphate of zinc itself, there is a provision, in the single constitutional atom of water of that salt, for the formation, by replacement, of the double sulphate of zinc and potash, and in the water of crystallization of the same salt, provision for the formation of various subsalts containing excess of oxide of zinc or ammonia, by similar replacements. The assumed molecular structure of the metal, thus leads to a farther development of the extending law of substitution.

The peculiarities of iron, by which it is enabled to resist amalgamation, to assume magnetism, to exhibit an indifference to nitric acid in certain circumstances, must depend upon the molecular structure of that metal, and are subjects which the chemist approaches with advantage when unfettered by the electrical hypothesis.

GENERAL SUMMARY.

1. No chemical affinity has been observed to act inductively, but that kind which has been described as operating in the voltaic circle. The affinity between two salts, the affinity of one metal for another, of one metal for a free non-metallic element, &c., appear to be incapable of acting in this way; or it may be that we have not the means of observing the inductive mode of action of these affinities. The action of the circles which have been formed of organic matters, such as slices of brain and beet-root, or the combinations of acid, alkali, and salts, employed by Becquerel, are too minute and obscure, to interfere with this general conclusion. That arrangement also of pairs of thin discs of positive and negative metals, with paper between each pair, which is known as the *dry pile*, acts only, it is admitted, when damp, and therefore when oxidation of the positive metal may occur.

2. The exciting compound or zincolyte must have a polar molecule, which requires it to consist of single zincous and chlorous atoms.

3. The molecules of the zincolyte must also have mobility and be able to assume a polar arrangement, or place themselves with their unlike and attractive poles together, so as to form a polar chain. This necessitates fluidity of the zincolyte (Faraday).

4. Of the metallic portions of the circle, the molecule is indifferently polarizable, that is, either side of it indifferently may become chloro-polar or zinco-polar, according to the direction of the induction affecting it. Hence these portions of the circle need not be fluid like the zincolytes.

5. In a closed voltaic circle, a certain number of lines or chains of polarized molecules is established, each chain being continuous round the circle. Hence the polar condition of the circle must be every where the same. The same number of particles of exciting fluid are simultaneously polar upon the surface of every zinc plate in the active cells, and also upon the surface of the zincoïd in the cell of decomposition, and the consequent chemical change, or decomposition occurring, is of the same amount in the same time in all the cells. Such equality in condition and results is essential to a *rotal* induction, such as exists in the voltaic circle.

The number of polar chains that can be established at the same time in a particular voltaic arrangement, is obviously affected by several circumstances :

(1) By the size of the zinc plate ; the number of particles of zinc that may be simultaneously acted upon by the exciting fluid, being directly proportional to the extent of metallic surface exposed.

(2) By the nature and accidental state of the exciting liquid, some zincolytes being more easily acted on by the positive metal than others ; while the state of dilution, temperature, and other circumstances may affect the facility of decomposition of any particular zincolyte.

(3) The adhesion of the gas bubbles of hydrogen to the copper plate, at which they are evolved, interferes much with the action of a battery. By taking up the hydrogen, by means of a solution of sulphate of copper in contact with the copper plate, Mr. Daniell increased the amount of circulating force six times.

(4) The chemical action in a cell is also diminished by increasing the distance from each other in the exciting fluid of the positive and negative metals.

(5) The lines of chemico-polar molecules in the exciting fluid should be repulsive of each other, like lines of magneto-polar elements, as illustrated in the mutual repulsion and divergence of the threads of steel filings which attach themselves to the pole of a magnet (Fig. 9.) That the lines of induction do diverge greatly in the acid, starting from the zinc as a centre, is placed beyond doubt by many experiments of Mr. Daniell. A small ball of zinc suspended in a hollow copper globe filled with acid, is the arrangement in which this divergence is least restrained, and was found to be the most effective form of the voltaic circle. When the copper too, is a flat plate, and wholly immersed in the acid, the back is found to act as a negative surface, as well as the face directly exposed to the zinc, showing that the lines of induction in the acid expand and open out from each other, some bending round the edge of the copper plate and terminating their action, after a second flexure, on its opposite side. To collect these diverging lines, the surface of the copper may be increased with advantage to at least four times that of the zinc.

(6) The polar chains of molecules, in the connecting wires and other metallic portions of the circle, must be equally repulsive of each other. Hence the small size of the negative plates in the active cells, and of the platinum plates in the cell of decomposition, and the thinness of the connecting wires, are among the circumstances which diminish the number of polar lines that can be established, and impair the general efficiency of a battery.

6. The effect of multiplying the active cells in a battery is not to increase the number of polar chains, or *quantity* of induced particles, but to increase the *intensity* of the induction in each chain; although this increase in intensity generally augments the quantity also, in an indirect manner, by overcoming more or less completely such obstacles to induction as have been enumerated.

7. The intensity of the induction, also, is much greater with some zincolytes than others. Thus a single pair of zinc and platinum plates excited by dilute sulphuric acid, decompose iodide of potassium, proto-chloride of tin and fused chloride of

silver, but not fused nitre, chloride or iodide of lead or solution of sulphate of soda. With the addition, however, of a little nitric acid to the sulphuric, the same single circle decomposes all these bodies, and even water itself. The evolution of hydrogen gas on the negative metal is at the same time suppressed by the nitric acid, which exerts a secondary action on that element.

8. The division of the connecting wire, and the separation of its extremities to the most minute distance from each other, is sufficient to stop all induction and the propagation of the polar condition. In the most powerful voltaic battery ever arranged, that which Mr. Daniell lately operated with, consisting of seventy of his large cells, no induction was observed to pass when the terminal wires were separated, not more than the one thousandth of an inch, even with the flame of a spirit-lamp or rarified air between them. Absolute contact of the wires was necessary to establish the circulation. But after contact was made, and the wires were heated to whiteness, they might be separated to a small distance without the induction being interrupted; the space between them was then filled with an arch of dazzling light, containing detached particles of the wire in a state of intense ignition, which were found to proceed from the zincoid to the chloroid, the former losing matter, and the other acquiring it. So highly fixed a substance as platinum is carried from pole to pole in this manner; but the transference of matter is most remarkable between charcoal poles, which may be separated to the greatest distance, and afford the largest and most brilliant arch of flame. A similar, although it may be an excessively minute detachment of matter, is found to accompany the electric spark in all circumstances. Hence, the electric spark always contains matter.

9. When terminal wires of a voltaic circle are grasped in the hands, the circuit may be completed by the fluids of the body, provided the battery contains a considerable number of cells and the induction is of high intensity; the nervous system is then affected, the sensation of the electric shock being experienced.

10. The conducting wire becomes heated precisely in proportion to the number of polar chains established in it, and consequently in proportion to the size of the zinc plate; and

this to the same degree from the induction of a single cell, as from any number of similar cells. Wires of different metals are unequally heated, according to the resistance which they offer to induction. The following numbers express the heat evolved by the same circulation in different metals, as observed by Mr. Snow Harris.

	Heat evolved.	Resistance.
Silver . . .	6	1
Copper . . .	6	1
Gold . . .	9	1½
Zinc . . .	18	3
Platinum . . .	30	5
Iron . . .	30	5
Tin . . .	36	6
Lead . . .	72	12
Brass . . .	10	3

The conducting powers of the metals are inversely as these numbers; silver being a better conductor than platinum in the proportion of 5 to 1. The conducting power of all of them is found to be diminished by heat.

11. As a portion of the voltaic circle, the conducting wire acquires extraordinary powers of another kind, which can only be very shortly stated here, belonging as they properly do to physics.

(1) Another wire placed near, and parallel to the conducting wire has the polar condition of its molecules disturbed, and an induction propagated through it in an opposite direction to that in the conducting wire.

(2) If the conducting wire be twisted in the manner of a cork-screw so as to form a hollow spiral or helix, it will be found in that form to represent a magnet, one end of the helix being a north, and the other a south pole; and, if moveable, will arrange itself in the magnetic meridian, under the influence of the earth's magnetism. Its poles are attracted by the unlike poles of an ordinary magnet, and it imparts magnetism to soft iron or steel by induction. Two such helices attract and repel each other by their different poles, like two magnets. Indeed an ordinary magnet may be viewed as a body having a helical chain of its molecules in a state of permanent chemico-polarity.

(3) If a bar of soft iron bent into the form of a horse shoe, with a copper wire twisted spirally round it, be applied like a lifter to the poles of a permanent magnet, in the instant of the iron becoming a magnet by induction, the molecules of the spiral wire become chemico-polar, and when contact is broken with the permanent magnet, and the soft iron ceases to be a magnet, the wire exhibits a polarity the reverse of the former. By a proper arrangement, electric sparks and shocks may be obtained from the wire, while the soft iron included within it is being made and unmade a magnet. The magneto-electric machine, is a contrivance for this purpose, and is now coming to supersede the old electric machine, as a source of what is termed electricity of tension. Magnetic and electric effects are thus reciprocally produced from each other.

(4) When the pole of a magnetic needle is placed near the conducting wire, the former neither approaches nor recedes from the latter, but exhibits a disposition to *revolve round it*. The extraordinary and beautiful phenomena of electrical rotation are exhibited in an endless variety of contrivances and experiments. As the magnetic needle is generally supported upon a pivot, it is free to move only in a horizontal plane, and consequently when the conducting wire is held over or under it (the needle being supposed in the magnetic meridian), the poles in beginning to describe circles in opposite directions round the wire, proceed to move to the right and left of it, and thus deviate from the true meridian. The amount of deviation in degrees is proportional to the quantity of circulating induction; and may be taken to represent it, as is done in a useful instrument, the galvanometer, to be afterwards described. It was in the form of these deflections, that the phenomena exhibited by a magnet, under the influence of a conducting wire, first presented themselves to Oersted in 1819.

FIG. 22.



12. Thermo-electrical phenomena are produced from the effect of unequal temperature upon metals in contact. If heat be applied to the point *c*, (Fig. 22.) at which two bars of bismuth and antimony *b* and *a* are soldered together, on connecting the free extremities by a wire, the whole is found to form a weak voltaic circle, with the induction from *b*

through the wire to *a*. Hence in this thermopolar arrangement the bismuth is the negative metal, and may be compared to the copper in the voltaic cell. If cold instead of heat be applied to *c*, a current also is established, but in an opposite direction to the former. Similar circuits may be formed of other metals, which may be arranged in the following order, the most powerful combination being formed of those metals which are most distant from each other in the following enumeration : bismuth, platinum, lead, tin, copper or silver, zinc, iron, antimony. When heated together, the current proceeds through the wire from those which stand first to the last. According to Nobili, similar circuits may be formed with substances of which the conducting power is lower than that of the metals.

Several pairs of bismuth and antimony bars may be associated as in Fig. 23, and the extreme bars being connected

FIG. 23.



by a wire, form an arrangement resembling a compound voltaic circle. Upon heating the upper junctions, and keeping the lower ones cool, or on heating the lower ones and keeping the others cool, an induction is established in the wire, more in-

tense than in the single pair of metals, but still very weak. The conducting wire strongly affects a needle, causing a deflection proportional to the inequality of temperature between the ends of the bars. Melloni's thermo-multiplier is a delicate instrument of this kind, which is even more sensitive to changes of temperature than the air thermometer, and has afforded great assistance in exploring the phenomena of radiant heat (page 32).

In such a compound bar, also, unequal temperature may be produced, by making it the connecting wire of a single and weak voltaic circle; whereupon the metals become cold at their junction, if the induction is from the bismuth to the antimony, and hot at the same point if the induction is in the opposite direction. These are the converse of the preceding phenomena, in which electrical effects were produced by inequality of temperature.

13. The friction of different bodies is another source of electrical phenomena. One, at least, of the bodies rubbed together must not be a conductor, and in general, two non-

conductors are used. When a silk handkerchief or a piece of resin is rubbed upon glass, both are found, after separation, in a polar condition, and continue in it. The rubbing surface of the glass is zinco-polar, and that of the resin or silk is chloro-polar, and a molecular polarization is at the same time established through the whole mass of both the glass and resin, reaching to their opposite surfaces, which exhibit the other polarity. The powers thus appearing on the two rubbing surfaces, being manifestly different, were distinguished by the names of the bodies on which they are developed, that upon the glass as *vitreous* electricity (zincous affinity), and that upon the resin as *resinous* electricity (chlorous affinity).

In comparing the chemico-polarity excited by friction with that of the voltaic circle, we observe that the former is of high intensity but small in quantity, or affecting only a small number of trains of molecules. If both the excited vitreous and resinous surfaces have a conducting metal, such as a sheet of tin-foil applied to them, and each sheet have a wire proceeding from it, the wires and tin-foil are polarized similarly to the glass and the resin which they cover, and a zincolyte placed between the extremities of the wires, which are respectively a zincoid and chloroid, is polarized also, and decomposed. But the amount of decomposition, which is a true measure of the *quantity* of induced particles, is extremely minute compared with the amount of induction in the voltaic circle. Thus, Mr. Faraday has calculated that the decomposition of one grain of water by zinc in the active cell of the voltaic circle, produces as great an amount of polarization and decomposition in the cell of decomposition, as 950,000 charges of a large Leyden battery, an enormous quantity of power, equal to a most destructive thunder storm. The polarization from friction is therefore singularly intense, although remarkably deficient in quantity, or in the number of molecules affected.

The kinds of matter susceptible of this intense polarization are so many, and so various, such as glass, minerals, wood, resins, sulphur, oils, air, &c., as to make it difficult to suppose that the polar molecule is of the same chemical constitution in all of them, as it is in the zincolytes of the voltaic circle. Indeed it must be admitted that all matter whatever may be forced into a polar condition, by a most intense in-

duction. Under such influence, too, the molecule appears to be indifferently polar.

Electrical induction at a distance, Mr. Faraday has shewn to be always an action of contiguous particles, chains of particles of air, or some other "dielectric," extending between the excited body which is inducing, and the induced body. His investigation of this subject led to the remarkable discovery that the intensity of electric induction at a constant distance from the inducing body, is not always the same, but varies in different media, the induction through a certain thickness of shell-lac, for instance, being twice as great as through the same thickness of air. Numbers may be attached to different bodies which express their relative inductive capacities:—

Specific inductive capacity of air	.	.	1
"	"	glass	. 1.76
"	"	shell-lac	. 2
"	"	sulphur	. 2.24

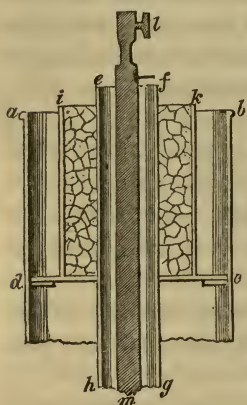
The inductive capacity of all gases is the same as that of air, and this property, it is remarkable, does not alter in these bodies with variations in their density.

VOLTAIC INSTRUMENTS.

Voltaic battery.—The working forms of the battery are too numerous to be individually noticed. That form only need be particularly described which is the most nearly perfect, and which in experiments of research is likely to supersede all others,—the *constant battery* of Mr. Daniell. A cell of this battery consists of a cylinder of copper $3\frac{1}{2}$ inches in diameter, which experience has proved to the inventor to afford the most advantageous distance between the metallic surfaces, but which may vary in height from 6 to 20 inches, according to the power which it is wished to obtain. A membranous bag formed of the gullet of an ox, is hung in the centre by a collar and circular copper plate, resting upon a rim within and near the top of the cylinder; and in this is suspended by a wooden cross bar, a cylindrical rod of amalgamated zinc half an inch in diameter. The outer cell is charged with a mixture of 8 measures or water and one of oil of vitriol, which has been saturated with

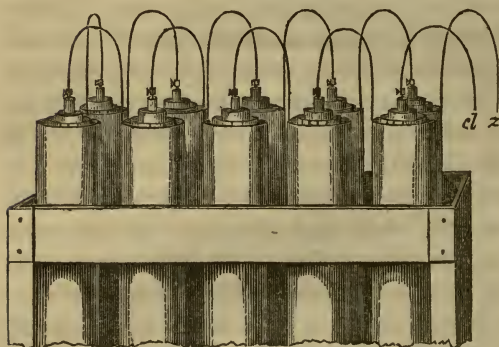
sulphate of copper, and portions of the solid salt are placed upon the circular copper plate, which is perforated like a colander, for the purpose of keeping the solution always in a state of saturation. The internal tube is filled with the same acid mixture without the salt of copper. A tube of porous earthenware, shut at the bottom, may be substituted for the membrane with great convenience, but Mr. Daniell believes with some little loss of power. A section of the upper part of one of these cells is here represented, *a b c d* is (Fig. 24) the external

FIG. 24.



copper cylinder; *e f g h*, the internal cylinder of earthenware, and *l m* the rod of amalgamated zinc. Upon a ledge *c d*, within an inch or two of the top of the cylinder, rests the cylindrical colander *i k*, which contains the copper salt, and both the sides and bottom of which are perforated with holes. A number of such cells may be connected into a compound circuit, with wires soldered to the copper cylinders, and fastened to the zinc by clamps and screws as shewn below. Fig. 25. (Daniell's Introduction to Chemical Philosophy, page 440.)

FIG. 25.



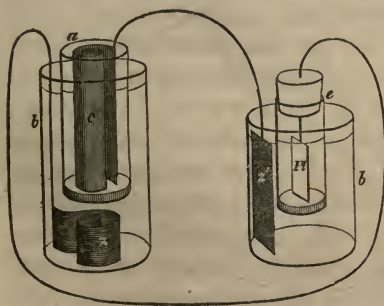
In this instrument the sulphate of zinc, formed by the solution of the zinc rod, is retained in the membranous bag or stoneware cylinder, and prevented from diffusing to the copper surface; while the hydrogen, instead of being evolved as gas on the surface

of the latter metal, decomposes the oxide of copper of the salt there, and occasions a deposition of metallic copper on the copper plate. Such a circle will not vary in its action for hours together, which makes it invaluable in the investigation of voltaic laws. It owes its superiority prin-

cipally to three circumstances:—to the amalgamation of the zinc, which prevents the waste of that metal by solution when the circuit is not completed; to the non-occurrence of the precipitation of zinc upon the copper surface; and to the complete absorption of the hydrogen at the copper surface, the adhesion of globules of gas to the metallic plates greatly diminishing, and introducing much irregularity into the action of a circle.

Bird's battery and decomposing cell.—To M. Becquerel we are particularly indebted for the investigation of the decomposing powers of feeble currents, sustained for a long time, the results of which are of extreme interest, both from the nature of the substances that can be thus decomposed, and from the form in which the elements of the body decomposed are presented, the slow formation of these bodies permitting their deposition in regular crystals.* Dr. Golding Bird has also added to the number of bodies decomposed by such means, and contrived a simple form of the battery, which with Becquerel's decomposing cell, renders such decompositions certain and easy, and forms indeed the voltaic instrument, perhaps above all others, the most directly useful to the chemist.† The decomposing cell

FIG. 26.



consists of a glass cylinder *a*, (Fig. 26) within another glass cylinder *b*. The inner cylinder *a* is 4 inches long and $1\frac{1}{2}$ inch in diameter, and is closed at the lower end by a plug of plaster of Paris 0.7 inch in thickness: this cylinder is fixed by means of wedges of cork within the other, which is a plain jar, about 8 inches deep

by 2 inches in diameter. A piece of sheet copper *c*, 4 inches long and 3 inches wide, having a copper conducting wire soldered to it, is loosely coiled up and placed in the inner cylinder with the plaster bottom: a piece of sheet zinc *z*, of equal size, is also loosely coiled, and placed in the outer cylinder; this zinc likewise being furnished with a conducting wire. The

* *Traité Expérimental de l'Electricité et du Magnétisme*, par M. Becquerel.

† *Phil. Trans.* 1837, p. 37.

outer cylinder is then nearly filled with a weak solution of common salt, and the inner with a saturated solution of sulphate of copper. The two fluids are prevented from mixing by the plaster diaphragm, and care being taken that they are at the same level in both the cylinders, the circle will afford, on joining the wires, a continuous current for weeks, the chloride of sodium and the sulphate of copper being very slowly decomposed. After it has been in action for some weeks, chloride of zinc is found in the outer cylinder; and beautiful crystals of metallic copper, frequently mixed with the ruby suboxide (closely resembling the native copper ruby ore), with large crystals of sulphate of soda, are found adhering to the copper plate in the smaller cylinder, especially on that part where it touches the plaster diaphragm.

The decomposing cell is the counterpart of the battery itself, consisting like it, of two glass cylinders, one within the other, the smaller one *c* having a bottom of plaster of Paris fixed into it: this smaller tube may be about $\frac{1}{2}$ inch wide and 3 inches in length, and is intended to hold the metallic or other solution to be decomposed, the external tube *d*, in which the other is immersed being filled with a weak solution of common salt. In the latter solution a slip of amalgamated zinc-plate *z'*, soldered to the wire coming from the copper plate *c* of the battery, is immersed; and a slip of platinum foil *pl*, connected with the wire from the zinc plate *z* of the battery, is immersed in the liquor of the smaller tube, being held in its place by a cork, through which its wire passes. The whole arrangement is now obviously a pair of active cells, of which *c z'* is one metallic element, and *z pl* the other; and the fluid between *z* and *c* divided by the porous plaster diaphragm, one fluid element, and the fluid between *z* and *pl*, divided by a porous plaster diaphragm, another fluid element; although it will be convenient to speak of the last as the cell of decomposition. With a solution of chlorides or nitrates of iron, copper, tin, zinc, bismuth, antimony, lead or silver, in the smaller tube, Dr. Bird finds the metals to be reduced upon the surface of the platinum, generally but not invariably in possession of a perfect metallic lustre, always more or less crystalline and often very beautifully so. The crystals of copper rival in hardness and malleability, the finest specimens of native copper, and those of silver, which are needles, are white and very brilliant. The solution of fluoride

of silicon in alcohol being introduced into the small tube by Dr. Bird, a deposition of silicon upon the platinum was found to take place in 24 hours, which was nearly black and granular and is described as exhibiting a tendency to a crystalline form. From an aqueous solution of the same fluoride, a deposition of gelatinous silica was observed to take place around the reduced silicon, mixed with which, or precipitated in a zone on the sides of the tube, especially if of small diameter, frequently appear minute crystalline grains of silica or quartz, of sufficient hardness to scratch glass, and appearing translucent under the microscope. With a modification of the decomposing cell described, Dr. Bird succeeded in decomposing a solution of chloride of potassium, and obtained an amalgam of potassium. The inner tube *c*, was replaced by a small glass funnel, the lower opening of which was stopt with stucco, and which thus closed retained a weak solution of the alkaline chloride poured into it. Every thing external to this funnel remaining as usual, mercury contained in a short glass tube, like a thimble, was placed in the funnel, and covered by the liquid, and instead of the platinum plate, a platinum wire coiled into a spiral at the extremity, was plunged into the mercury, the other end of this wire being connected with the zinc plate *z*, of the battery. The circuit having been thus completed, the mercury had swollen in eight or ten hours to double its former bulk, and when afterwards thrown into distilled water, evolved hydrogen and produced an alkaline solution. A solution of hydrochlorate of ammonia being substituted for that of chloride of potassium, in this experiment, the metal swells to 5 or 6 times its bulk in a few hours, and the semifluid amalgam of ammonium is formed. These feeble currents thus effect decompositions, in the lapse of time, which batteries of the ordinary form and considerable magnitude, may effect very imperfectly, or fail entirely in producing.

Volta-meter.—The decomposing power of a battery is represented by the quantity of oxygen and hydrogen gases evolved in a cell of decomposition containing dilute sulphuric acid. The volta-meter is simply a cell so charged, and of a proper form to allow of the gases evolved being collected and measured. One of the simplest forms is that constructed for me by Mr. Young. It is a stout eight ounce phial (Fig. 27), through the cork of which two platinum wires are passed, with flat plates

of platinum attached to them within the bottle, which become the terminal plates of the battery when its wires are thrust into the cavities of two small hollow brass cylinders attached externally to the platinum wires of the apparatus. The gases escape by a bent glass tube fitted into the cork of the bottle, and may be collected in a graduated jar at a small pneumatic trough. In this instrument steel plates may be substituted for the platinum, provided a solution of carbonate of potash be used instead of dilute sulphuric acid.

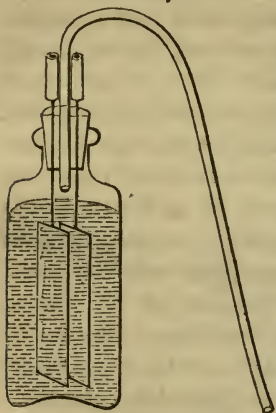
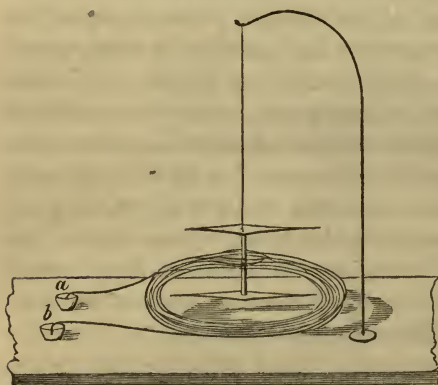


FIG. 27.

Galvanometer.—The sensibility of the magnetic needle to the influence of the conducting wire of a voltaic circle brought near it, has been applied to the construction of an instrument which will indicate the feeblest polarization or slightest current in the connecting wire. It consists of a pair of magnetic needles (Fig. 28,) fixed on one axis with their

FIG. 28.



attracting poles opposite each other, so as to leave them little or no directive power and render them astatic, which is delicately suspended by a single fibre of unspun silk. The lower needle is enclosed within a circle formed by a hank of covered wire, of which the extremities *a* and *b* terminate in little cups containing mercury. When the terminal wires of a battery are introduced into the same cups, the hank of wire of the galvanometer becomes part of the connecting wire, and the needle is deflected. The inductions proceeding in one direction above the needle and returning in the opposite direction below needle, conspire to produce the same deflection; and the upper needle having its poles reversed, is deflected in the same

direction, by the wire below it, as the lower needle is by the wire above it. Every turn of the wire also, repeats the influence upon the needle, so that the deflection is increased in proportion to the number of turns or coils in the hank of wire.

PART II.

CHAPTER I.

NON-METALLIC ELEMENTS.

SECTION I.

OXYGEN.

Equivalent 100, or 8 on hydrogen scale; symbol O; density 1102.6 (air = 1000); combining measure \square (one volume.)

THE following thirteen of the fifty-five elementary bodies known are included in the class of non-metallic elements:—oxygen, hydrogen, nitrogen, carbon, boron, silicon, sulphur, selenium, phosphorus, chlorine, bromine, iodine, and fluorine. Of these, oxygen, from certain relations which it bears to all the others, and from its general importance, demands our first attention.*

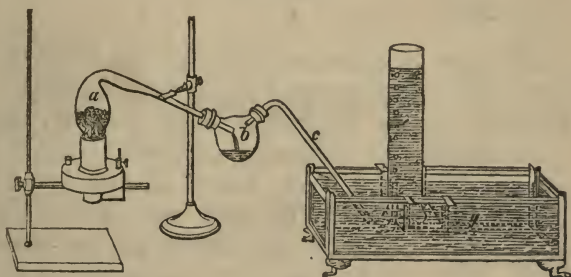
The name oxygen is compounded of $\alpha\acute{\xi}\nu\varsigma$ acid, and $\gamma\epsilon\nu\nu\alpha\omega$ I generate, and was given to the element of which I am about to treat by Lavoisier, with reference to its property of forming acids in uniting with other elementary bodies. Oxygen is a permanent gas, when uncombined, and forms one fifth part of the air of the atmosphere. In a state of combination, this element is the most extensively diffused body in nature, entering as a constituent into water, into nearly all the earths and rocks of which the crust of the globe is composed, and into all organic products with a very few exceptions. It was first recognised as a distinct substance by Dr. Priestley in this country, in 1774, and about a year afterwards by Scheele in Sweden, without any knowledge of Priestley's experiments. From this discovery may be dated the origin of true chemical theory.

* To the class of metals an addition has recently been made by the discovery of Latane, which makes the 55th elementary body. (An. de Ch. et de Ph. t. 70, p. 222.)

Preparation.—Oxygen gas is generally disengaged from some compound containing it, by the action of heat.

1°. It was first procured by Priestley, by heating red precipitate (peroxide of mercury,) which is thereby resolved into fluid mercury and oxygen gas. To illustrate the formation of oxygen in this way, 200 grains of red precipitate may be introduced into the body of a small retort *a* of hard or difficultly

FIG. 29.



fusible glass, and the retort united in an air-tight manner with a small globular flask *b*, having two openings, both closed by perforated corks, one of which admits the beak of the retort, and the other an exit tube *c*, of glass, bent as in the figure. The extremity of the exit tube is introduced into a graduated jar *d*, capable of holding 50 or 60 cubic inches, and placed in an inverted position, full of water upon the shelf of a pneumatic water-trough. Heat is then applied to the retort, by means of an Argand spirit lamp, powerful enough to raise it to a red heat, and maintain it at that temperature for a considerable time. The first effect of the heat is to expand the air in the retort, bubbles of which issue from the tube *c*, and rise to the top of the jar *d*, displacing water; but more gas follows, which is oxygen, and at the same time metallic mercury condenses in the neck of the retort and runs down into the intermediate flask *b*. When the red precipitate in the retort has entirely disappeared, the lamp may be extinguished, and the retort allowed to cool completely. The end of the exit tube *c* being now above the level of the water in the jar, which is nearly full of gas, a portion of the latter, equal in bulk to the air which first left the retort, will return to it, from the contraction of the gas within the retort. The jar will be found in the end to contain 48 cubic inches of gas, which is therefore the measure

of oxygen produced in the experiment, and the flask to contain 184 grains of mercury. Now 48 cubic inches of oxygen weigh 16 grains; and a true analysis of the red precipitate has been effected, of which the result is, that 200 grains of that substance consist of—

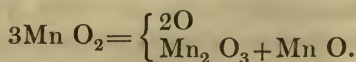
184 grains mercury.	
16 „ oxygen, (48 cubic inches.)	
<hr/>	
200	

But oxygen gas is more generally derived from two other substances, oxide of manganese and chlorate of potash.

2°. When the gas is required in large quantity, and exact purity is immaterial, the oxide of manganese is preferred from its cheapness. This is a black, heavy mineral found in Devonshire and other parts of England, and of which upwards of 40,000 tons are consumed annually in the manufactures of the country. It is called an oxide of manganese, because it is a compound of the metal manganese with oxygen. In explanation of what takes place when this substance is heated, it is necessary to state that manganese is capable of uniting with oxygen in several proportions, namely one equivalent, or 346 parts of manganese, with 100, and with 200 parts of oxygen, and two equivalents of manganese with 300 oxygen. These compounds are:—

Protoxide of manganese	. . .	$Mn + O.$
Deutoxide	$2Mn + 3O.$
Peroxide, or native black oxide	. . .	$Mn + 2O.$

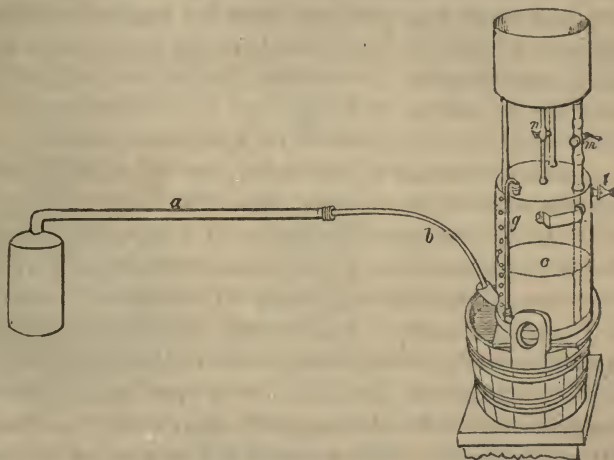
Now the peroxide however strongly heated, never loses more than one third of its oxygen, being converted into a compound of the first two oxides, that is, three equivalents of peroxide (1638 parts) lose two equivalents of oxygen (200 parts), and leave a compound of one of deutoxide and one of protoxide; a change which may be thus expressed:—



One of the malleable iron bottles in which mercury is imported, is readily converted into a retort, in which the black oxide may be heated, by removing its screwed iron stopper, and re-

placing this by an iron pipe of three feet in length, one end of which has been cut to the screw of the bottle. This pipe may be bent like *a* in the figure, if the bottle is to be heated

FIG. 30.



in an open fire or in a furnace open at the top. From 3 to 9 pounds of the oxide may be introduced as a charge, according to the quantity of gas to be prepared, each pound of the best Exeter manganese yielding about 1400 cubic inches, or 5.05 gallons of gas. Upon the first application of heat, water comes off, as steam, mixed with a gas which extinguishes flame; this is owing to the impurity of the oxide. The products may be allowed to escape, till the point of a wood-match red without flame, applied to the orifice, is not completely extinguished, but rekindled and made to burn with brilliancy; the gas is then sufficiently pure, and means must be taken for collecting it. A small flexible lead tube *b*, of any convenient length is adapted to the iron pipe, by means of a perforated cork, by which the gas is conveyed to a pneumatic trough, and collected in glass jars filled water, as in the former experiment; or, as this process affords considerable quantities of oxygen, the gas is more generally conducted into the inferior cylinder or drum of a copper gas holder *c*, full of water. The water does not flow out by the recurved tube which forms the lower opening, but is retained in the vessel by the pressure of the atmosphere on the surface of the water in that tube, as

water is retained in a bird's drinking glass. But when the lead tube is introduced into the gas-holder by this opening, water escapes by it, in proportion as gas is thrown into the cylinder, and rises in bubbles to the top. The progress of filling the gas-holder may be observed by the glass gauge tube *g*, which is open at both ends, and connected with the top and bottom of the cylinder, so that the water stands at the same height in the tube as in the cylinder. Convenient dimensions for the cylinder itself are 16 inches in height by 12 in diameter; to fill which a charge of three pounds of manganese may be used. The gauge tube is so apt to be broken, or to occasion leakage at its junctions with the cylinder, when the latter is large and unwieldy, that it is generally better to forego the advantage it offers, and dispense with this addition to the gas-holder. When applied to a small gas-holder, the ends of the tube are conveniently adapted to the openings of the cylinder, by means of perforated corks, which are afterwards covered with melted sealing-wax.

After the cylinder is filled, the lower opening by which the gas was admitted is closed by a good cork, or by a brass cap made to screw over it. The superior cylinder is an open water trough, connected with the inferior cylinder by two tubes provided with stopcocks, *m* and *n*, one of which *m* is continued to the bottom of that vessel, and conveys water from the superior cylinder, while the other tube *n*, terminates at the top of the inferior cylinder, and affords a passage by which the gas can escape from it, when water is allowed to descend by the other

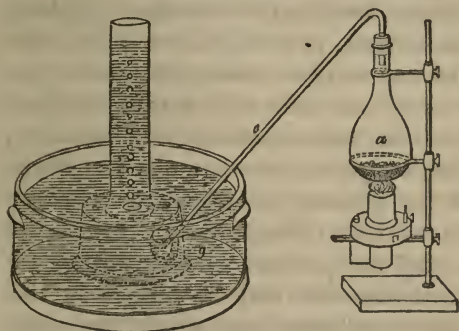


FIG. 31. tube. The tube and perforation of the stopcock of *m* should be considerably wider than *n*. A jar *a* is filled with gas by inverting it full of water in the superior cylinder, over the opening of *n*, as exhibited in the figure, and allowing the gas to ascend from the inferior cylinder. Gas may likewise be obtained by the stopcock *l* (Figure 30) water being allowed to enter by *m* at the same time.

Oxygen may likewise be disengaged from oxide of manganese in a flask or retort, by means of sulphuric acid diluted with an equal bulk of water, but this is not a process to be recommended. When only a small quantity of oxygen is required, it is better to have recourse to chlorate of potash, which has also the advantage of giving a perfectly pure gas.

3°. A well cleansed Florence oil flask, the edges of the mouth of which have been heated and turned over so as to form a lip, with a bent glass tube and perforated cork fitted to it, as in the figure, forms a convenient retort in which about half an ounce of chlorate of potash may be heated by means of the Argand spirit lamp. The salt melts, although it

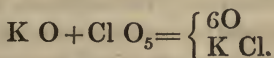
FIG. 32.



contains no water, and when nearly red hot, emits abundance of oxygen gas. At one point of the decomposition, the effervescence may become so violent as to burst the flask, especially if the exit tube be narrow, unless the heat be moderated.

The chlorate of potash

parts with all the oxygen it possesses, which amounts to 37 per cent. of its weight, and leaves a white hard salt, the chloride of potassium. From an atomic statement of the composition of this salt, one equivalent of it (1532 parts) will be observed to contain six equivalents of oxygen (600 parts), five in the chloric acid and one in the potash, the whole of which come off, leaving an equivalent of chloride of potassium (932 parts) :—



Half an ounce of chlorate of potash should yield 270 cubic inches or nearly a gallon of pure oxygen gas.

Properties.—Oxygen gas is colourless, and destitute of odour and taste. It is heavier than air in the ratio of 1102.6 to 1000 according to the weighings of Dulong and Berzelius; 100 cubic inches of air being taken to weigh 31 grains at the temperature of 60° and with the barometer at 30 inches, 100 cubic inches of oxygen gas will therefore weigh 34.18 grains. One cubic inch weighs 0.3418 or very nearly 1-3rd of a grain. It has never been liquefied by cold or pressure. Oxygen is so sparingly soluble in water, that when agitated in contact with that fluid no perceptible diminution of its volume takes place. But when water is previously deprived of air by boiling, 100

cubic inches of it dissolve three and a half cubic inches of this gas.

If a lighted wax taper attached to a copper wire be blown out, and dipped into a vessel of oxygen gas, while the wick remains red hot, it instantly rekindles with a slight explosion, and burns with great brilliancy. If soon withdrawn and blown out, it may be revived again in the same manner, and the experiment be repeated several times in the same gas. Lighted tinder burns with flame in oxygen, and red-hot charcoal with brilliant scintillations. Burning sulphur introduced into this gas in a little hemispherical cup of iron-plate with a wire attached to it, burns with an azure blue flame of considerable intensity. Phosphorus introduced into oxygen in the same manner, burns with a dazzling light of the greatest splendour, particularly after the phosphorus boils and rises through the gas in vapour. Indeed all bodies which burn in air, burn with increased vivacity in oxygen gas. Even iron wire may be burned in this gas. For this purpose thin harpsichord wire should be coiled about a cylindrical rod into a spiral form. The rod being withdrawn, a piece of thread must be twisted about one end of the wire, and dipped into melted sulphur; the other end of the wire is to be fixed into a cork, so that the spiral may hang vertically. The sulphured end is then to be lighted, and the wire suspended in a jar of oxygen, open at the bottom, such as that represented in Fig. page 246, supported upon an earthenware plate. The wire is kindled by the sulphur, and burns with an intense white light, throwing out a number of sparks, or occasionally allowing a globule of fused oxide to fall; while the wire itself continues to fuse and burn till it is entirely consumed, or the oxygen is exhausted. This experiment forms one of the most beautiful and brilliant in chemistry. The globules of fused oxide are of so elevated a temperature, that they remain red-hot for some time under the surface of water, and fuse deeply into the substance of the stoneware plate upon which they fall.

Oxygen gas is respirable, and indeed is constantly taken into the lungs from the atmosphere in ordinary respiration. When a portion of dark blood drawn from a vein is agitated with this gas, the colour becomes of a fine vermilion red. The same change occurs in the blood of living animals, during respiration, from the absorption of oxygen gas, which is believed

to maintain the animal heat in part. A small animal, also, such as a mouse or bird, lives four or five times longer in a vessel of oxygen than it will in an equal bulk of air. But the continued respiration of this gas in a state of purity is injurious to animal life. A rabbit is found to breathe it without inconvenience for some time, but after an interval of an hour or more, the circulation and respiration are much quickened; and a state of great excitement of the general system supervenes; this is by and by followed by debility, and death occurs in from six to ten hours. The blood is found to be highly florid in the veins as well as the arteries, and the heart, according to Broughton, continues to act strongly after the breathing has ceased.

Oxygen may be made to unite with all the other elements except fluorine, and forms *oxides*, while the process of uniting with oxygen is termed *oxidation*. With the same element oxygen often unites in several proportions, forming a series of oxides, which are then distinguished from each other by the different prefixes enumerated under *chemical nomenclature* (page 98.) Many of its compounds are *acids*, particularly those which contain more than one equivalent of oxygen to one of the other element, and compounds of this nature are those which it most readily forms with the non-metallic elements, such as carbonic acid with carbon, sulphurous acid with sulphur, phosphoric acid with phosphorus. But oxygen unites in preference with single equivalents of a large proportion of the metallic class of elements, and forms bodies which are alkaline or have the character of *bases*, such as potash, lime, magnesia, protoxide of iron, &c. A certain number of its compounds are neither acid nor alkaline, and are therefore called *neutral* bodies, such as the oxide of hydrogen or water, carbonic oxide, and nitrous oxide. The greater number of these neutral oxides are also protoxides.

It has already been stated that in a classification of the elements oxygen does not stand alone, but forms one of a small natural family along with sulphur, selenium and tellurium (page 142.) These elements also form acid, basic and neutral classes of compounds, with the same bodies as oxygen does, of which the sulphur compounds are well known, and always exhibit a well-marked analogy to the corresponding oxides. Oxygen acids unite with oxygen bases, and form neutral *salts*, so do sulphur acids with sulphur bases, selenium acids

with selenium bases, and tellurium acids with tellurium bases.

The combinations of oxygen, like those of all other bodies, are attended with the evolution of heat. This result, which is often overlooked in other combinations, in which the proportions of the bodies uniting and the properties of their compounds receive most attention, assumes an unusual degree of importance in the combinations of oxygen. The economical applications of the light and heat evolved in these combinations are of the highest consequence and value, and oxidation alone of all chemical actions is practised, not for the value of the products it affords, and indeed without reference to them, but for the sake of the incidental phenomena attending it. Of the chemical combinations too, which we habitually witness, those of oxygen are infinitely the most frequent, which arises from its constant presence and interference, as a constituent of the atmosphere. Hence, when a body combines with oxygen it is said to be *burned*; and instead of undergoing oxidation, it is said to suffer *combustion*; and a body which can combine with oxygen and emit heat is termed a *combustible*. Oxygen, in which the body burns, is then said to support combustion, and called a *supporter* of combustion.

The heat evolved in combustion is definite, and can be measured. With this view, it is employed to melt ice, to raise the temperature of water from 32° to 212° , or to convert water into steam, and its quantity estimated by the extent to which it produces these effects. The heat from the oxidation of a combustible body is thus found to be as constant as any other of its properties. Despretz obtained, by such experiments, the results contained in the following table:—

HEAT FROM COMBUSTION.

1 pound of pure charcoal	heats from 32° to 212° , 78	lbs. of water.
charcoal from wood	75	" "
baked wood	36	" "
wood containing 20 per cent. of water	27	" "
bituminous coal	60	" "
turf	25 to 30	" "
alcohol	67.5	" "
olive oil, wax, &c.	90 to 95	" "
ether	80	" "
hydrogen	236.4	" "

The quantity of heat evolved appears to be connected with

the proportion of oxygen consumed, for the greater the weight of oxygen with which a pound of any combustible unites, the more heat is produced. The following results indicate that the heat depends exclusively upon the oxygen consumed, four different combustibles in consuming a pound of oxygen affording nearly the same quantity of heat:—

HEAT FROM COMBUSTION.

1 pound of oxygen with hydrogen heats from 32° to 212°, 29½ lbs. of water.

"	"	with charcoal	"	"	"	29	"	"
"	"	with alcohol	"	"	"	28	"	"
"	"	with ether	"	"	"	28½	"	"

The quantity of combustible consumed in these experiments varied considerably, but the oxygen being the same, the heat evolved was nearly the same also. But when the same quantity of oxygen converted phosphorus into phosphoric acid, exactly twice as much heat was evolved, according to Despretz, as in the former experiments. It is doubtful whether these observations will lead to any general conclusions; but it is certain that the coincidences which they exhibit merit attention. The superior vivacity of the combustion of these and other bodies in pure oxygen, compared with air, depends entirely upon the increased rapidity of the process, and the larger quantity of combustible oxidated in a given time. A candle burns with more light and heat in oxygen than in air, but it consumes proportionally faster.

Oxidation is often a very slow process and imperceptible in its progress, as in the rusting of iron and tarnishing of lead exposed to the atmosphere. The heat being then evolved in a very gradual manner is dissipated and never accumulates. But when the oxide formed is the same, the nature of the change effected is no way altered by its slowness. Iron oxidates rapidly when introduced in a state of ignition into oxygen gas, and lead, in the form of the lead pyrophorus, which contains that metal in a state of high division, takes fire spontaneously and burns in the air, circumstances then favouring the rapid progress of oxidation.

Oxidation may also go on with a degree of rapidity sufficient to occasion a sensible evolution of heat, but without flame and open combustion. The absorption of oxygen by spirituous liquors in becoming acetic acid, and by many other organic substances,

is always attended with the production of heat. The smouldering combustion of iron-pyrites and some other metallic ores in the atmosphere, is a phenomenon of the same nature. Most bodies which burn with flame, also admit of being oxidated at a temperature short of redness, and exhibit the phenomenon of *low combustion*. Thus, tallow thrown upon an iron plate not visibly red-hot, melts and undergoes oxidation, diffusing a pale lambent flame only visible in the dark (Dr. C. J. B. Williams). If the tallow be heated in a little cup with a wire attached, till it boils and catches fire, and the flame then be blown out, the hot tallow will still continue in a state of low combustion, of which the flame may not be visible, but which is sufficient to cause the renewal of the high combustion, if the cup is immediately introduced into a jar of oxygen gas. A candle newly blown out is sometimes rekindled in oxygen, although no point of the wick remains red, owing to the continuance of this low combustion. When a coil of thin platinum wire, or a piece of platinum foil is first heated to redness and then held over a vessel containing ether or hot alcohol, the vapours of these substances, mixed with the air, oxidate upon the hot metallic surface, and may sustain the metal at a red heat for a long time, without the occurrence of combustion with flame. The product, however, of the low combustion of these bodies is peculiar, as is obvious from its pungent odour.

Combustion in air.—The affinity for oxygen of all ordinary combustibles is greatly promoted by heating them, and is indeed rarely developed at all except at a high temperature. Hence, to determine the commencement of combustion, it is commonly necessary that the combustible be heated to a certain point. But the degree of heat necessary to inflame the combustible, is in general greatly inferior to what is evolved during the progress of the combustion, so that a combustible, once inflamed, maintains itself sufficiently hot to continue burning till it is entirely consumed. Here the difference may be observed between combustion and simple ignition. A brick heated till it is red-hot in a furnace, and taken out, exhibits ignition, but has no means within itself of sustaining a high temperature, and soon loses the heat which it had acquired in the fire, and on cooling is found unchanged. The oxidable constituents of wood, coal, oils, tallow, wax, and all the ordinary combustibles are the same, carbon and hydrogen, which

in combining with oxygen, at a high temperature, always produce carbonic acid and water, which being volatile disappear, forming part of the heated aerial column that rises from the burning body. The constant removal of the product of oxidation, thus effected by its volatility, greatly favours the progress of combustion in such bodies, by permitting the free access of air to the unconsumed combustible. The interference of air in combustion is obvious from the facility with which a fire is checked or extinguished when the supply of air is lessened or withheld, and, on the contrary, revived and animated when the supply of air is increased by blowing upon it. For the oxygen of the air being consumed in combining with the combustible, a constant renewal of it is necessary. Hence, if a lighted taper, floated by a cork upon water, be covered with a bell jar having an opening at top, such as that in which the iron-wire was burned, the taper will burn for a short time without change, then more and more feebly, in proportion as the oxygen is exhausted, and at last will expire. The air remaining in the jar is no longer suitable to support combustion, and a second lighted taper introduced into it by the opening at top, is immediately extinguished.

In combustion, no loss whatever of ponderable matter occurs; nothing is annihilated. The matter formed may always be collected without difficulty, and is found to have exactly the weight of the oxygen and combustible together which have disappeared. The most simple illustrations of this fact are obtained in the combustion of those bodies, which afford a solid product. Thus when 2 grains of phosphorus are kindled in a measured volume of oxygen gas, they are found converted after combustion into a quantity of white powder (phosphoric acid), which weighs $4\frac{1}{2}$ grains, or the phosphorus acquires $2\frac{1}{2}$ grains; at the same time $7\frac{1}{2}$ cubic inches of oxygen disappear which weigh exactly $2\frac{1}{3}$ grains. In the same way when iron wire is burned in oxygen, the weight of solid oxide produced is found to be equal to that of the wire originally employed added to that of the oxygen gas which has disappeared. But the oxidation of mercury affords a more complete illustration of what occurs in combustion. Exposed to a moderate degree of heat for a considerable time in a vessel of oxygen, that metal is converted into red scales of oxide, which possess the additional weight of a certain volume of oxygen which has disappeared.

But if the oxide of mercury, so produced, be then put into a small retort, and reconverted by a red heat into oxygen and fluid mercury, the quantity of the oxygen emitted is found to be the same as had combined with the mercury in the first part of the operation, thus proving that oxygen is really present in the oxidized body.

The evolution of heat, which is the most striking phenomenon of combustion, still remains to be accounted for. It has been referred to the loss of latent heat by the combustible and oxygen, when, from the condition of gas or liquid, they become solid after combustion; to a reduction of capacity for heat, the specific heat of the product being supposed to be less than that of the bodies burned; to a discharge of the electricities belonging to the different bodies, occurring in the act of combination. But the first two hypotheses are manifestly insufficient, and the last is purely speculative. The evolution of heat during intense chemical combination, such as oxidation, may be received at present as an ultimate fact; but if we choose to go beyond it, we may suppose that the heat exists in a combined and latent state in either the oxygen or combustible, or in both, that each of these bodies is a compound of its material bases with heat, the whole or a definite quantity of which they throw off on combining with each other. Heat, like other material substances, is here supposed, not to evince its peculiar properties while in a state of a combination with other matter, but only when isolated and free. This view gives a literal character to the expressions, liberation, disengagement, and evolution of heat during combustion. The phenomenon, it is to be remembered, is not confined to oxidation, but occurs in an equal degree in combinations without oxygen, and indeed to a greater or less extent in all chemical combinations whatever.

Uses.—Pure oxygen has not as yet found any considerable application in the arts. But by the chemist it is applied to support the combustion of hydrogen gas, in producing intense heat. A more considerable application of it is likely to arise in the combustion of oil in the lamp of Mr. Gurney, to produce an intense light suitable for marine light-houses. In this lamp, which is an Argand with several concentric wicks, oxygen gas from a gasometer is admitted into the centre of the flame, and is found to produce so much more light than air does, from the combustion of the same quantity of oil, as fully to compensate

for the cost of the oxygen. Where a large quantity of oxygen is required, as in this application of it, the gas may be obtained by heating oxide of manganese in a cylinder of cast iron supported over a furnace, like the retort for coal gas. The calcined oxide does not regain its oxygen when afterwards exposed to the air, as was once supposed, but would still be of some value in the preparation of chlorine.

SECTION II.

HYDROGEN.

Equivalent 12.5 (oxygen 100), or 1 as the bases of the hydrogen scale; symbol H; density 69 (air 1000); combining measure $\square\square$ (two volumes.)

Hydrogen gas, which was long confounded with other inflammable airs, was first correctly described by Cavendish, in 1766. It does not exist uncombined in nature, at least the atmosphere does not contain any appreciable proportion of hydrogen. But it is one of the elements of water, and enters into nearly every organic substance. Its name is derived from $\upsilon\delta\omega\rho$, water, and $\gamma\epsilon\nu\nu\alpha\omega$, I generate, and refers to its forming water when oxidated.

Preparation.—This element, although resembling oxygen in being a gas, appears to be more analogous to a metal in its chemical properties. By heating oxide of mercury, we have seen it resolved into oxygen and mercury; and several other metallic oxides, such as those of silver and gold, are susceptible of a similar decomposition. But some others are deprived of only a portion of their oxygen by the most intense heat, such as peroxide of manganese; and many, such as the protoxide of lead, are not decomposed at all by simple calcination. By igniting the latter oxide, however, mixed with charcoal, its oxygen goes off in combination with carbon, as carbonic oxide, and the lead is left. The oxide of hydrogen or water is in the same case. Heat alone does not decompose it. But potassium and sodium brought into contact with it, at the temperature of the air, combine with its oxygen, and are converted into the oxides potash and soda; and hydrogen is consequently liberated, water being the oxide of hydrogen.

Iron and many other metals decompose water, and become oxides, at a red heat. Hence, hydrogen gas is sometimes procured by transmitting steam through an iron tube placed across a furnace and heated red-hot. Some other compounds of hydrogen are decomposed more easily than water, by iron and zinc. The chloride of hydrogen or hydrochloric acid is decomposed by these metals, and evolves hydrogen, at the ordinary temperature of the air. But this gas is more generally obtained by putting pieces of zinc or iron into oil of vitriol or the concentrated sulphuric acid, diluted with 6 or 8 times its bulk of water. The hydrogen is then derived from the decomposition of the proportion of water intimately united with the acid, as illustrated in the following diagram, zinc being used, and the quantities expressed:—

Before decomposition.		After decomposition.	
613½	oil of vitriol, or sulphate of water. . .	{ Hydrogen . . . 12½ 12½ hydrogen. Oxygen . . . 100 Sulphuric acid 501	
403	zinc . . .	Zinc . . . 403	1004 sulphate of oxide of zinc.
<hr/> 1016½		<hr/> 1016½	<hr/> 1016½

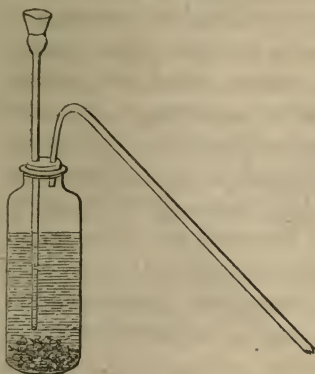
Or by symbols:—



The zinc dissolves in the acid with effervescence, from the escape of hydrogen gas. It will be observed that the products after decomposition, mentioned in the last column, hydrogen and sulphate of oxide of zinc are similar to those before decomposition, in the first column, zinc and sulphate of water; and that the change occurring is simply the *substitution* of zinc for hydrogen in the sulphate of water. The large quantity of water used with the acid is useful to dissolve the sulphate of zinc formed.

Zinc is generally preferred to iron, in the preparation of hydrogen, and is previously granulated, by being fused in a stone-ware crucible, and poured into water; if sheet zinc be used, it must be cut into small pieces. The common glass retort may be used in the experiment, or a gas-bottle, such as the half pound phial (Fig. 33), with a cork having two perforations fitted with glass tubes, one of which descends to the

FIG. 33.



bottom of the bottle, and is terminated externally by a funnel for introducing the acid, whilst the other is the exit tube, by which the hydrogen escapes. With an ounce or two of zinc in it, the bottle is two-thirds filled with water, and the undiluted acid added from time to time by the funnel, so as to sustain a continued effervescence. No gas escapes by the funnel tube, as its extremity within the bottle is

always covered by the fluid. To produce large quantities, a half-gallon stone-ware jar may be mounted as a gas bottle, with a flexible metallic pipe fitted to the cork, as the exit tube. This gas may be collected, like oxygen, either in jars over the pneumatic trough, or in the gas-holder. The first jar or two filled will contain the air of the gas-bottle, and therefore must not be considered as pure hydrogen. One ounce of zinc is found to cause the evolution of 615 cubic inches of hydrogen.

Properties.—Hydrogen gas thus prepared is not absolutely pure, but contains traces of sulphuretted hydrogen and carbonic acid, which may be removed by agitating the gas with lime-water or caustic alkali. It has also a particular odour, which is not essential to hydrogen, as the gas evolved from the amalgam of sodium, acted on by pure water without acid, is perfectly inodorous. An oily compound of carbon and hydrogen, which appears to be the cause of this odour, may be separated in a sensible quantity from the gas prepared by iron, by transmitting it through alcohol. Of the pure gas, water does not dissolve more than $1\frac{1}{2}$ per cent. of its bulk. Hydrogen has never been liquefied by cold or pressure.

Hydrogen is the lightest substance in nature, being sixteen times lighter than oxygen, and 14.4 times lighter than air; 100 cubic inches of it weigh only 2.14 grains. Soap bubbles blown with this gas ascend in the atmosphere; and it is used, as is well known, to inflate balloons, which begin to rise when the weight of the stuff of which they are made and the hydrogen together, are less than the weight of an equal bulk of air. A light bag is prepared for making this experiment in the chamber,

by distending the lining membrane of the crop of the turkey, which may weigh 35 or 36 grains, and when filled with hydrogen, about 5 grains more, or 41 grains; the same bulk of air, however, would weigh 50 or 51 grains; so that the little balloon when filled with hydrogen has a buoyant power of 9 or 10 grains. Sounds produced in this gas were found by Leslie to be extremely feeble, much more feeble indeed than its rarity compared with air could account for. Hydrogen may be taken into the lungs without inconvenience, when mixed with a large quantity of air, being in no way deleterious; but it does not, like oxygen, support respiration, and therefore an animal placed in pure hydrogen soon dies of suffocation. A lighted taper is extinguished in this gas.

Hydrogen is eminently combustible, and burns when kindled in the air with a yellow flame of little intensity, which moistens a dry glass jar held over it; the gas combining with the oxygen of the air in burning, and producing water. If before being kindled the gas is first mixed with enough of air to burn it completely, or with between two and three times its volume, and then kindled, the combustion of the whole hydrogen is instantaneous and attended with explosion. With pure oxygen instead of air the explosion is much more violent, particularly when the gases are mixed in the proportions of two volumes of hydrogen to one of oxygen, which are the proper quantities for combination. The combustion is not thus propagated through a mixture of these gases, when either of them is in great excess. The sound in such detonations is occasioned by the concussion which the atmosphere receives from the sudden dilatation of gaseous matter, in this case of steam, which is prodigiously expanded from the heat evolved in its formation. A musical note may be produced by means of these detonations, when they are made to succeed each other very rapidly. If hydrogen be generated in a gas bottle, and kindled as it escapes from an upright glass jet having a small aperture, the gas will be found to burn tranquilly; but on holding an open glass tube of about two feet in length over the jet, like a chimney, the flame will be elongated and become flickering. A succession of little detonations is produced, from the gas being carried up and mixing with the air of the tube, which follow each other so quickly as to produce a continuous sound or musical note.

Several circumstances affect the combination of hydrogen with oxygen, which are important. These gases may be mixed together in a glass vessel, and preserved for any length of time without combining. But combination is instantly determined by flame, by passing the electric spark through the mixture, or even by introducing into it a glass rod, not more than just visibly red-hot. Hydrogen, indeed, is one of the more easily inflammable gases. If the mixed gases be heated in a vessel containing a quantity of pulverized glass, or any sharp powder, they begin to unite in contact with the foreign body in a gradual manner without explosion, at a temperature not exceeding 660°. The presence of metals disposes them to unite at a still lower temperature; and of the metals, those which have no disposition of themselves to oxidate, such as gold and platinum, occasion this slow combustion at the lowest temperature. In 1824, Dobereiner made the remarkable discovery that newly prepared spongy platinum has an action upon hydrogen independently of its temperature, and quickly becomes red-hot when a jet of this gas is thrown upon it in air, combination of the gases being effected by their contact with the metal. In consequence of this ignition of the platinum the hydrogen itself is soon inflamed, as it issues from the jet. An instrument depending upon this action of platinum has been constructed for producing an instantaneous light. More lately Mr. Faraday observed that the divided state of the platinum, although favourable, is not essential to this action; and that a plate of that metal, if its surface be scrupulously clean, will cause a combination of the gases, accompanied with the same phenomena, as the spongy platinum. This action of platinum is manifested at temperatures considerably below the freezing point of water, and in an explosive mixture largely diluted with air or hydrogen. Spongy platinum, made into pellets with a little pipe-clay, and dried, when introduced into mixtures of oxygen and hydrogen, will be found to cause a gradual and silent combination of the gases, in whatever proportions they are mingled, which will not cease till one of them is completely exhausted. The theory of this effect of platinum is very obscure. It belongs to a class of actions depending upon surface, not confined to that metal, and by which other combustible vaporous bodies are affected besides hydrogen (page 196.)

The flame of hydrogen, although so slightly luminous, is in-

tensely hot; few combinations producing so high a temperature, as the combustion of hydrogen. In the oxi-hydrogen blow-pipe, oxygen and hydrogen gases are brought by tubes from different gas-holders, and allowed to mix immediately before they escape by the same orifice, at which they are inflamed. This is most safely effected by fixing a jet for the oxygen within the jet of hydrogen, so that the oxygen is introduced into the middle of the flame of hydrogen, a construction first proposed by Mr. Maugham, and adapted to the use of coal gas instead of hydrogen by Mr. Daniell.* At this flame the most refractory substances, such as pipe-clay, silica and platinum, are fused with facility, and the latter even dissipated in the state of vapour. The flame itself, owing to the absence of solid matter, is scarcely luminous, but any of the less fusible earths, upon which it is thrown, a mass of quick-lime for instance, is heated most intensely, and diffuses a light, which for whiteness and brilliancy may be compared to that of the sun. With a requisite supply of the gases this light may be sustained for hours, care being taken to move the mass of lime slowly before the flame, so that the same surface may not be long acted upon; for the high irradiating power of the lime is soon impaired, it is supposed from a slight agglutination of its particles occasioned by the heat. This light placed in the focus of a parabolic reflector, was found to be visible, in the direction in which it was thrown, at a distance of 69 miles, in one experiment made by Mr. Drummond, when using it as a signal light. The heating effects are even more intense when the gases are forced into a common receptacle, and allowed to escape from under pressure, but there is the greatest risk of the flame passing back through the exit tube and exploding the mixed gases, an accident which would expose the operator to the greatest danger. Mr. Hemming's apparatus, however, may be used without the least apprehension. A common bladder is used to hold the mixture, and the gas before reaching the jet, at which it is burned, is made to pass through his safety tube. This consists of a brass cylinder about six inches long and 3-4ths of an inch wide, filled with fine brass wire of the same length, which is tightly wedged by forcibly inserting a pointed rod of metal into the centre of the bundle. The conducting power of the metallic channels

* Phil. Mag. 3rd Series, vol. II, p. 57.

through which the gas has then to pass is so great as completely to intercept the passage of flame.

Hydrogen is capable of forming two compounds with oxygen, namely water, which is the protoxide, and the peroxide of hydrogen.

Uses.—The most important of the present applications of hydrogen gas is in the oxi-hydrogen blow-pipe. It has been superseded as a material for inflating balloons, by coal gas, the balloon being proportionally enlarged to compensate for the less buoyancy of the latter gas.

PROTOXIDE OF HYDROGEN.—WATER.

Equivalent 112.5, or 9 on hydrogen scale ; *formula* $H + O$, or $H O$; *density* 1, as steam 620.2 (air 1000) ; *combining measure of steam* .

Mr. Cavendish first demonstrated, in 1781, that the product of the combustion of hydrogen and oxygen is water. He burned known quantities of these gases in a dry glass vessel, and found that water was formed in quantity exactly equal to the weights of the gases which disappeared. It was afterwards established by Humboldt and Gay-Lussac, that the gases unite rigorously in the proportion of two volumes of hydrogen to one volume of oxygen, and that the water produced by their union occupies, while it remains in the state of vapour, exactly two volumes (page 131). The proportion of the constituents of water by weight was determined with extraordinary care by Berzelius and Dulong. Their method was to transmit dry hydrogen gas over a known weight of the black oxide of copper, contained in a glass tube, and heated to redness by a lamp. The gas was afterwards conveyed through another weighed tube containing the hygrometric salt, chloride of calcium. The hydrogen gas in passing over the oxide of copper, combines with its oxygen and forms water, which is carried forward by the excess of hydrogen gas, and absorbed in the chloride of calcium tube. The weight of this water being ascertained, the proportion of oxygen it contains is determined by ascertaining the loss which the oxide of copper has sustained; the difference is the hydrogen. The mean of three such experiments gave as the composition of water :

Oxygen	.	88.9	or	100	or	8.009
Hydrogen	.	11.1	„	12.48	„	1.
		<hr/>		<hr/>		<hr/>
		100		112.48		9.009

The oxygen and hydrogen are therefore very nearly, if not exactly, in the proportion of 8 to 1, as appears by the proportions of the last column. This experiment serves not only to determine rigorously the composition of water, but it offers also the best method of ascertaining the composition of such metallic oxides as are de-oxygenated by hydrogen.

Properties.—When cooled down to 32° water freezes, if in a state of agitation, but may retain the liquid condition at a lower temperature, if at rest (page 40) ; the ice, however, into which it is converted cannot be heated above 32° without melting. Ice is lighter than water, its specific gravity being 0.916 ; and the form of its crystal is a rhomboid, very nearly resembling iceland spar. Water is elastic and compressible, yielding according to Oersted 53 millionths of its bulk to the pressure of the atmosphere, and, like air, in proportion to the compressing force for different pressures. The peculiarities of its expansion by heat while liquid, have already been fully described (page 8). Under a barometric pressure of 30 inches, it boils at 212°, but evaporates at all inferior temperatures. Its boiling point is elevated by the solution of salts in it, and the temperature of the steam from these solutions is not constantly 212°, as has been alleged, but that of the last strata of liquid through which the steam has passed. When mixed with air, the vapour of water has a tendency to condense in vesicles, which inclose air ; forming in this condition the masses of clouds, which remain suspended in the atmosphere from the lightness of the vesicles, the substance of mists and fogs, and “ vapour ” generally, in its popular meaning. The vesicles may be observed by a lens of an inch focal length, over the dark surface of hot tea or coffee, mixed with an occasional solid drop which contrasts with them. According to the experiments of Saussure, made upon the mists of high mountains, these vesicles generally vary in size from the 1-4500th to the 1-2780th of an inch, but are occasionally observed as large as a pea. They are generally condensed by their collision into solid drops, and fall as rain ; but their precipitation in that form is much retarded in some conditions of the atmosphere.

A cubic inch of water at 62° , Bar. 30 inches, weighs in air 252.458 grains. The imperial gallon has been defined to contain 10 pounds avoirdupois (70,000 grains) of distilled water at that temperature and pressure. Its capacity is therefore 277.19 cubic inches. The specific gravity of water at 60° is 1, being the unit to which the densities of all other liquids and solids are conveniently referred; it is 815 times heavier than air at that temperature.

In its chemical relations water is eminently a neutral body. Its range of affinity is exceedingly extensive, water forming definite compounds, to all of which the name *hydrate* is applied, with both acids and alkalies, with a large proportion of the salts, and indeed with most bodies containing oxygen. It is also the most general of all solvents. Gay-Lussac has observed that the solution of a salt is uniformly attended with the production of cold, whether the salt be anhydrous or hydrated, and that on the contrary, the formation of a definite hydrate is always attended with heat: a circumstance which indicates an essential difference between solution, and chemical combination*. Even the dilution of strong solutions of some salts, such as those of ammonia, occasions a fall of temperature. The solvent power of water for most bodies increases with its temperature. Thus at 57° water dissolves one fourth of its weight of nitre, at 92° one half, at 131° an equal weight, and at 212° twice its weight of that salt. Solutions of such salts, saturated at a high temperature, deposit crystals on cooling. But the crystallization of some saturated solutions is often suspended for a time, in a remarkable manner, and afterwards determined by slight causes. Thus, if three pounds of crystallized sulphate of soda be dissolved in two pounds of water, with the assistance of heat, and the solution be filtered while hot, through paper, to remove foreign solid particles, and then set aside in a glass matrass, with a few drops of oil on its surface, it may become perfectly cold without crystallization occurring. Violent agitation even may not cause it to crystallize. But when any solid body, such as the point of a glass rod, or a grain of salt, is introduced into the solution, crystals immediately begin to form about the solid nucleus, and shoot out in all directions through the liquid. The solubility of many

* An. de Ch. et de Phys. t. 70 p. 407. See also page 180 of this work.

salts of soda and lime does not increase with the temperature, like that of other salts.

Water is also capable of dissolving a certain quantity of air and other gases, which may again be expelled from it by boiling the water, or by placing it in vacuo. Rain-water generally affords $2\frac{1}{2}$ per cent of its bulk of air, in which the proportion of oxygen gas is so high as 32 per cent, and in water from freshly melted snow 34.8 per cent, according to the observations of Gay-Lussac and Humboldt, while the oxygen in atmospheric air does not exceed 21 per cent. Boussingault finds that the quantity of air retained by water, at an altitude of 6 or 8000 feet, is reduced to one third of its usual proportion. Hence it is that fishes cannot live in Alpine lakes, the air contained in the water not being in adequate quantity, for their respiration. The following table exhibits the absorbability of different gases by water deprived of all its air by ebullition :

100 cubic inches of water at 60° and 30 Bar., absorb of

	Dalton and Henry.	Saussure.
Sulphuretted hydrogen .	100 C. I.	253
Carbonic acid . .	100 .	106
Nitrous oxide . .	100 .	76
Olefiant gas . . .	12.5 .	15.3
Oxygen . . .	3.7 .	6.5
Carbonic oxide . .	1.56 .	6.2
Nitrogen . . .	1.56 .	4.1
Hydrogen . . .	1.56 .	4.6

The results of Saussure are probably nearest the truth, for sulphuretted hydrogen and nitrous oxide, but for the other gases those of Dalton and Henry are most to be depended on.

Uses.—Rain received after it has continued to fall for some time may be taken as pure water, excepting for the air it contains. But after once touching the soil, it becomes impregnated with various earthy and organic matters, from which it can only be completely purified by distillation. A copper still should be used for that purpose, provided with a copper or block tin worm, which is not used for the distillation of spirits, as traces of alcohol remaining in the worm and becoming acetic acid, cause the formation of acetate of copper, which would be washed out and contaminate the distilled water. The use of white lead

cement about the joinings of the worm is also to be avoided, as the oxide of lead is readily dissolved by distilled water. The first portions of the distilled water should be rejected, as they often contain ammonia, and the distillation should not be carried to dryness.

Water employed for economical purposes is generally submitted to a more simple process, that of filtration, by which it is rendered clear and transparent by the removal of matter mechanically suspended in it. Such foreign matter may often be removed in a considerable degree by subsidence, on which account it is desirable that the water should stand at rest for a time, before being filtered. The filtration of liquids generally is effected on the small scale, by allowing them to flow through unsized or filter paper, and that of water, on the large scale, by passing it through beds of sand. The sand preferred for that purpose is not fine, but gravelly, and crushed cinders or furnace clinkers may be substituted for it. Its function, as that also of the paper in the chemist's filter, is to act as a *support* for the finer particles of mud or precipitate which are first deposited on its surface, and form the bed that really filters the water. When the mud accumulates so as to impede the action of the sand filter, the surface of the sand is scraped, and an inch or two of it removed. Upward filtration through a bed of sand is sometimes practised, but it has the disadvantage that the filter cannot be cleaned in the manner just indicated. Filtering under high pressure and with great rapidity has lately been practised in a very compact apparatus, consisting of a box, not above three feet square, filled with sand. This filter which becomes speedily choked with the mud it detains, is cleansed by suddenly reversing the direction in which the water is passing through the box, which occasions a shock that has the effect of loosening the sand, and allowing the water to bring away the mud. The action of such a filter, lately erected at the Hôtel-Dieu of Paris, has been favourably reported on by M. Arago*.

Matter actually dissolved in water is not affected by filtration. No repetition of the process would withdraw the salt from sea-water and make it fresh. Hence the impregnation of peaty matter, which river water generally contains, and to the greatest extent in summer, when the water is concentrated by evapo-

* An. de Ch. et de Ph. t. 65, p. 428.

ration, is not removed by filtering. Animal charcoal is the proper substance for discolouring liquids, as it withdraws organic colouring matter, even when in a state of solution.

In the process of clarifying liquors, by dissolving in them the white of egg and other albuminous fluids, the temperature is raised so as to coagulate the albumen, which thus forms a delicate net-work throughout the liquid, and is afterwards thrown up as scum in the boiling, carrying all the foreign matter suspended in the liquid along with it.

The most usual earthy impurities in water, occasioning its hardness, are sulphate of lime, and the carbonate of lime dissolved in carbonic acid, both of which are precipitated on boiling the water, and occasion an earthy incrustation of the boiler. When waters contain iron, they are termed *chalybeate*; this metal is most frequently in the state of carbonate dissolved in carbonic acid, and rarely in a proportion exceeding one grain in a pound of water. The *sulphureous* waters, which are recognized by their peculiar odour, and by blackening silver and salts of lead, contain sulphuretted hydrogen gas, in a proportion not exceeding the usual proportion of air in spring water, and no oxygen. *Saline* waters, for the most part contain various salts of lime and magnesia, and generally common salt. Their density is always considerably higher than that of pure water. *Sea-water* contains $3\frac{1}{2}$ per cent. of saline matter, and has a density 1.0274. Its composition is interesting, as the sea comes to be the grand depository of all the soluble matter of the globe. A most minute and valuable analysis of the water of the English Channel has lately been executed by Dr. Schweitzer of Brighton, the particulars of which I subjoin in contrast with an analysis of the water of the Mediterranean by M. Laurens:—

Sea-water of the English Channel.			Of the Mediterranean.		
	Grains.			Grains.	
Water . . .	964.74372	.	.	.	959.26
Chloride of sodium .	27.05948	.	.	.	27.22
— potassium .	0.76552	.	.	.	0.01
— magnesium	3.66658	.	.	.	6.14
Bromide of magnesium	0.02929	.	.	.	
Sulphate of magnesia .	2.29578	.	.	.	7.02
— lime . .	1.40662	.	.	.	0.15
Carbonate of lime .	0.03301	Carb. of lime & magn.			0.20
<hr/>			<hr/>		
1000.0000			1000.00		

These analyses shew that the channel water contains 9 times as much lime as the Mediterranean, but this can be accounted for, as the water flows over a bed of chalk. The Mediterranean, again, contains twice as much magnesia and sulphuric acid as the Channel. In addition to those constituents, distinct traces of iodine and of ammonia were detected.*

PEROXIDE OF HYDROGEN.

Equivalent, 212.5, or 17 on hydrogen scale ; formula $H + 2O$, or HO_2 .

The second compound of hydrogen and oxygen is a liquid, containing twice as much oxygen as water, and is a body possessed of very extraordinary properties. It was discovered by Thenard, in 1818, who prepared it by a long and intricate process.

Preparation.—The formation of the peroxide of hydrogen depends upon the existence of a corresponding peroxide of barium. The latter is obtained by calcining pure nitrate of barytes at a high temperature in a porcelain retort, and afterwards exposing the earth barytes or protoxide of barium, which is left, in a porcelain tube heated to redness, to a stream of oxygen gas, which the protoxide rapidly absorbs becoming peroxide. Treated with a little water the peroxide of barium slakes and falls to powder, forming a hydrate, of which the formula is $Ba O_2 + H O$. Dilute acids have a peculiar action upon this hydrate, which will be easily understood, if the peroxide of barium is represented as the protoxide united with an additional equivalent of oxygen, or as $Ba O + O$. They combine with the protoxide of barium, forming salts of barytes, and the second equivalent of oxygen, instead of being liberated in consequence, unites with the water of the hydrate, the HO of the preceding formula, giving rise to $HO + O$ or the peroxide of hydrogen, which dissolves in the water. Although it would be inconvenient to abandon the systematic name peroxide of hydrogen for this compound, still it must be allowed that the properties of the body, as well as its mode of preparation are more favourable to the idea of its being a combination of water with oxygen, or *oxygenated water*, as it was first named by its discoverer, than a direct combination of its elements. It is re-

* Phil. Mag. 3rd Series, vol. 15, page 58. (1839.)

commended by Thenard to dissolve the peroxide of barium in hydrochloric acid considerably diluted with water, and to remove the barytes by sulphuric acid, which forms an insoluble sulphate of barytes. The hydrochloric acid, again free in the liquor, is saturated a second time with peroxide of barium and precipitated; and after several repetitions of these two operations, the hydrochloric acid itself is removed by the cautious addition of sulphate of silver, and the sulphuric acid of the last salt by solid barytes. Such is an outline of the process; but its success requires attention to a number of minute precautions which are fully detailed in the *Traité de Chimie* of the author quoted.* The weak solution of peroxide of hydrogen, which this process affords, may be concentrated by placing it with a vessel of strong sulphuric acid under the receiver of an air pump, until the solution attains a density of 1.452, when the peroxide itself begins to rise in vapour without change. It then contains 475 times its volume of oxygen.

M. Pelouze abridges this process considerably by employing hydrofluoric acid or fluosilicic acid, in place of hydrochloric acid, to decompose the peroxide of barium. By this operation, the barytes separates at once with the acid, in the state of the insoluble fluoride of barium, and nothing remains in solution but the peroxide of hydrogen. After thus decomposing several portions of peroxide of barium successively in the same liquor, the fluoride of barium may be separated by filtration, and the peroxide of hydrogen, which is still dilute, be concentrated by means of the air-pump.

Properties.—Peroxide of hydrogen is a colourless liquid resembling water, but less volatile, having a metallic taste, and instantly bleaching litmus and other organic colouring matters. It is decomposed with extreme facility, effervescing from escape of oxygen at a temperature of 59° , and when suddenly exposed to a greater heat, such as 212° , actually exploding from the rapid evolution of the gas. It is rendered more permanent by dilution with water, and still more so, by the addition of the stronger acids, while alkalies have the opposite effect.

The circumstances attending the decomposition of this body are the most curious facts in its history. Many pure metals and metallic oxides occasion its instantaneous resolution into

* Vol. I, page 479 of the 6th edition.

water and oxygen gas, by simple contact, without undergoing any change themselves, affording a striking illustration of catalysis (page 196); and this decomposition may excite an intense temperature, the glass tube in which the experiment is made sometimes becoming red-hot. Some protoxides absorb at the same time a portion of the oxygen evolved, and are raised to a higher degree of oxidation, but most of them do not; and certain oxides, such as the oxides of silver and gold, are reduced to the metallic state, their own oxygen going off along with that of the peroxide of hydrogen. The decomposition of these metallic oxides cannot be ascribed to the heat evolved, for oxide of silver is reduced in a very dilute solution of the peroxide of hydrogen, although the decomposition is not then attended with a sensible elevation of temperature. The metallic oxides which are decomposed in this remarkable manner are originally formed by the decomposition of other compounds, and not by the direct union of their elements, which in fact exhibit little affinity for each other. In this general character, they agree with peroxide of hydrogen.

Uses.—The peroxide of hydrogen is a substance which it is exceedingly desirable to possess, with the view of employing it in bleaching, and for other purposes as a powerful oxidating agent. But the expense and uncertainty of the process for preparing this compound have hitherto prevented any application of it in the arts, or even its occasional use as a chemical reagent.

SECTION III.

NITROGEN.

Synonyme, AZOTE. Equiv. 177, or 14.2 on hydrogen scale; symbol N; density 976; combining measure □□.

Dr. Rutherford of Edinburgh examined the air which remains after the respiration of an animal, and found that after being washed with lime-water, which removes carbonic acid, it was incapable of supporting either combustion or respiration. He concluded that it was a peculiar gas. Lavoisier afterwards discovered that this gas exists in the air of the atmosphere, forming indeed 4-5ths of that mixture, and gave it the name azote, (from α , privative, and $\zeta\omega\eta$, life), from its inability to

support respiration. It was afterwards named nitrogen by Chaptal, because it is an element of nitric acid. Besides existing in air, nitrogen forms a constituent of most animal and of several vegetable substances. In a natural arrangement of the elements, nitrogen is placed next phosphorus, and in close relation with antimony and arsenic.

Preparation. — Nitrogen is generally procured by allowing a combustible body to combine with the oxygen of a certain quantity of air confined in a vessel. For that purpose a glass flask may be inverted over a small jet of hydrogen, burning as it issues from the upright exit tube of a gas bottle, till the flame goes out, which it does after exhausting the oxygen in the flask. The flask is then removed from the hydrogen bottle, its mouth being closed with the thumb, and conveyed to a pneumatic trough, where the residuary gas contained in the flask may be transferred into a jar. Or a little metallic or porcelain cup may be floated, by means of a cork, on the surface of the water-trough. A few drops of alcohol are then introduced into the cup, or a small piece of phosphorus is placed in it, and being kindled, a tall bell jar is held over the cup, with its lip in the water. The combustion soon terminates, and the water of the trough rises in the jar. Alcohol does not consume the oxygen entirely, a small portion of it still remains mingled with the nitrogen; a certain quantity of carbonic acid gas is also produced by its combustion. But the combustion of phosphorus exhausts the oxygen completely, and leaves nitrogen unmixed with any other gas. Nitrogen may likewise be obtained by several chemical decompositions, which, however, are more curious than important as sources of this gas. Chlorine gas, for instance, conducted into diluted ammonia, is absorbed and evolves nitrogen; so do fragments of sal ammoniac thrown into a solution of chloride of lime; fresh muscular flesh is also dissolved by nitric acid when heated, with the evolution of nitrogen.

Properties.—Nitrogen gas is tasteless and inodorous; has never been liquefied, and is less soluble in water than oxygen. It is a little lighter than air, which possesses the mean density of 79 volumes of nitrogen and 21 volumes of oxygen. Nitrogen is a singularly inert substance and does not unite directly with any other single element, so far as I am aware, under the influence of light or of a high temperature. A burning taper is

instantly extinguished in this gas, and an animal soon dies in it, not because the gas is injurious, but from the privation of oxygen, which is required in the respiration of animals. Nitrogen appears to be chiefly useful in the atmosphere, as a diluent of the oxygen, thereby repressing to a certain degree the activity of combustion and other oxidating processes. The evidence of the fixation of free nitrogen by plants is incomplete, and therefore it cannot be said with certainty that the nitrogen of the organic world is primarily derived from the atmosphere.* When heated with oxygen, nitrogen does not burn like hydrogen, nor undergo oxidation. But nitrogen may be made to unite with oxygen by transmitting several hundred electric sparks through a mixture of these gases in a tube, with water or an alkali present, and nitric acid is produced. The water formed by the combustion of hydrogen in air, or of a mixture of hydrogen and nitrogen in oxygen, has often an acid reaction, which is due to a trace of nitric acid. The same acid is also a product of the oxidation of a variety of compounds containing nitrogen. Ammonia mixed with air, on passing over spongy platinum at a temperature of about 572° , is decomposed, and the nitrogen it contains is completely converted into nitric acid, by combining with the oxygen of the air. Cyanogen and air, under similar circumstances, occasion the formation of nitric and carbonic acids.† Nitric acid is also largely produced by the oxidation of organic matters during putrefaction in air, when an alkali or lime is present, as in the natural nitre soils and artificial nitre beds.

A suspicion has always existed that nitrogen may be a compound body, but it has resisted all attempts to decompose it, and the evidence of its elementary character is equally good with that of most other bodies reputed simple. If the equivalent of nitrogen be divided by 3, a curious parallism is observed between some of its compounds, and those of oxygen with the same elements, to which attention has been directed by M. Laurent and by M. A. Bineau.‡ Before considering the compounds of nitrogen with oxygen, we may notice the properties of atmospheric air, which is regarded as a mechanical mixture of these gases.

* Boussaingault, *Ann. de Ch. et de Ph.* t. 67, p. 5, and 69, p. 353.

† Kuhlman, *Phil. Mag.* 3rd Series, vol. 14, page 157.

‡ *An. de Ch. et de Ph.* t. 67, p. 242.

THE ATMOSPHERE.

According to the careful experiments of Dr. Prout, 100 cubic inches of atmospheric air, deprived of aqueous vapour and the small quantity of carbonic acid it usually contains, weigh 31.0117 grains, at 60° and 30 Bar. Its density at the same temperature and pressure is estimated at 1000, and is conveniently assumed as the standard of comparison for the densities of gaseous bodies, as water is for solids and liquids. Hence, at 62°, air is 815 times lighter than water, and 11,065 times lighter than mercury. The bulk of air varies with its temperature and the pressure affecting it, according to the same laws as other gases (pages 11 and 66.)*

The mean pressure of the atmosphere at the surface of the sea is generally estimated as equal to the weight of a column of mercury of 30 inches in height, which is about 15 pounds on the square inch of surface, and is equivalent to a column of water of nearly 34 feet in height. The oxygen alone is equal to a column of 7.8 feet of water over the whole earth's surface, from which an idea may be formed of the immense quantity of that element, and how small the effect must be of the oxidating processes observed at the earth's surface in diminishing it. If the atmosphere were of uniform density its height, as inferred from the barometer, would be 11,065 times 30 inches, or 5.238 miles, but the density of air being proportional to the pressure upon it, diminishes with its elevation, the superior strata being always more rare and expanded than the inferior strata upon which they press.

* The rate of the expansion of gases by heat has lately been corrected by Rudberg, who finds that 1 volume of gas at 32° becomes 1.365 vol. at 212°, which gives a dilatation of 0.002028, or 1-493rd part, instead of 1-480th of the bulk at 32°, for each degree Fahrenheit. If the expansion be expressed in parts of the bulk at 0° Fahr. which is more convenient for calculation, the expansion is 1-461 part for each degree. The volume of a gas at 0° being 1, at any higher temperature it is

$$\text{always} = 1 + \frac{\text{Temp. Fahr.}}{461}.$$

DENSITY OF THE ATMOSPHERE.

Height above the sea in miles.	Volume.
0	1
2.705	2
5.41	4
8.115	8
10.82	16
13.525	32
16.23	64

At a height of 2.705 miles (11,556 feet) the atmosphere is of half density, by calculation, or 1 volume is expanded into 2, and the barometer would stand at 15 inches; the density is again halved for every 2.7 miles additional elevation. From calculations founded on the phenomena of refraction, the atmosphere is supposed to extend, in a state of sensible density, to a height of nearly 45 miles. It is certainly limited, but whether by the cold prevailing in its higher regions, which may liquefy or even solidify the aerial particles, or from their expansibility having a natural limit (page 18), is uncertain. The atmospheric pressure also varies at the same place, from the effect of winds and other causes, which are not fully understood. Hence, the use of the barometer as a weather glass; for wet and stormy weather is generally preceded by a fall of the mercury in the barometer, and fair and calm weather by its rise.

The temperature of the atmosphere is greatest at the earth's surface, and has been observed to diminish one degree for every 352 feet of ascent, in the lower strata. It is believed, however, that the progressive diminution is less rapid at great distances from the earth. But at a certain height, the region of perpetual congelation is attained even in the warmest climates; the summits of the Andes, which rise 21,000 feet, being perpetually covered with snow under the equator. The line of perpetual congelation, which has been fixed at 15,207 feet at 0° latitude, descends progressively in higher latitudes, being 3,818 feet at 60°, and only 1,016 feet at 75°. The decrease of temperature with elevation in the atmosphere is ascribed to two causes. 1°. To the property which air has of becoming cold by expansion, which arises from an increase of the latent heat of air, like that of steam, with rarefaction (page 54.) The actual

temperature of the different strata of the atmosphere is indeed believed to be that due to their dilatation, supposing that they had all the same original temperature and density as the lowest stratum. 20. To the circumstance that the atmosphere derives its heat principally from contact with the earth's surface. The sun's rays appear to suffer little absorption in passing through the atmosphere; but there are some observations on the force of solar radiation which are not easily reconciled with that circumstance. A thermometer, of which the bulb is blackened, rises a certain number of degrees above the temperature of the air, when exposed to sun, but the rise is decidedly greater on high mountains than near the level of the sea, and in temperate, or even arctic climates, which is more remarkable, than within the tropics. It is a question how solar radiation is obstructed in the hotter climates. (Daniell's Meteorological Essays, 2nd ed.)

The blue colour of the sky has been found by Brewster to be due to light that has suffered polarization, which is therefore reflected light, like the white light of clouds. The air of the atmosphere must therefore have a disposition to absorb the red and yellow solar rays and to reflect the blue rays. At great heights, the blue colour of the sky was observed by Theodore de Saussure to become deeper and deeper, being mixed with black, owing to the absence of white reflecting vesicular vapour or clouds. The red and golden tints of clouds appear to be connected with a remarkable property of steam lately discovered by Professor Forbes. A light seen at night through steam issuing into the atmosphere from under a pressure of from 5 to 30 pounds on the inch, is found to appear of a deep orange red colour, exactly as if observed through a bottle containing nitrous acid vapour. The steam, when it possesses this colour, is mixed with air, and on the verge of condensation; and it is known that the golden hues of sunset depend upon a large proportion of vapour in the air, and are indeed a popular prognostic of rain.*

The movement of masses of air, or wind, is always produced by inequality of temperature of the atmosphere at different points of the earth's surface, or in different regions of the atmosphere of equal elevation. The primary movement is always

* Phil. Mag. 3rd Series, vol. 14, pp. 121 and 425, and vol. 15, pp. 25, and 419.

an ascending current, the heated and expanded air over some spot rising in a vertical column. Dense and colder air flows towards that point producing the horizontal current which is remarked by an observer on the earth's surface. Some winds are of a very limited range, and depend upon local circumstances; such are the sea and land breeze experienced upon the coasts of tropical countries. From its low conducting power, the surface of the land is more quickly heated than the sea, so that soon after sunrise the expanded air over the former begins to ascend, and is replaced by the colder air from the sea, forming the sea breeze. But after sunset, the earth's heat being less in quantity, is more quickly dissipated by radiation than that of the sea, and the air over the land becomes dense and flows outwards, displacing the air over the sea, and producing the land breeze. It is obvious that these inferior currents must be attended by a superior current in an opposite direction, or that the air in these winds is carried in a perpendicular vortex of no great extent, of which the motion is reversed twice every twenty-four hours. A grand movement of a similar nature is produced in the atmosphere, from the high temperature of the equatorial compared with the polar regions of the globe; the air over the former constantly ascending, and having its place supplied by horizontal currents from the latter, within the lower region of the atmosphere. Hence, if the earth were at rest, the wind would constantly blow at its surface, from the poles to the equator, and in the opposite direction in the upper strata of the atmosphere. But the earth, accompanied by its atmosphere makes a diurnal revolution upon its axis, in which any point on its surface is always passing to a point in space previously to the east of it, and with a velocity proportional to its circle of latitude on the globe; a velocity which is consequently nothing at the poles, and attains its maximum at the equator. The result of this is, that the lower current or polar stream, in tending to the equator, is constantly passing over parallels of latitude which have a greater degree of velocity of rotation to the east, than the stream itself, which comes thus to be felt as a resistance from the east; and instead of appearing as a wind directly from the north as it really is, this stream appears as a wind from the east with a certain northerly declination, which diminishes as the stream approaches the equator, where it flows directly from the east, constituting the

great trade-wind which constantly blows across the Atlantic and Pacific Oceans from east to west within the tropics. Our keen east winds in spring have a low temperature which attests their arctic origin. The upper or equatorial current has its course deflected by similar causes; starting from the equator it has a greater projectile force to the east than the parallels of latitude over which it has to pass, and retaining this motion towards the east it appears, as it passes over them, a west wind or wind from the west. The upper current, flowing in the opposite direction from the trade-wind below, was actually experienced by Humboldt and Bonpland on the summit of the Peak of Teneriffe, and has been indicated at various times by the transport of volcanic ashes by its means.

On the great oceans, within the temperate zone, westerly winds prevail greatly over easterly, which are supposed by some to be the upper current descending to the surface of the earth. These westerly winds temper the climate of the western sea-board both of Europe and America, which is much milder than the climate of their eastern coasts.

The nature of the movement of the atmosphere in hurricanes has lately received considerable elucidation. It appears that they move in circles, and are great horizontal vortices, which are probably produced by currents of air meeting obliquely, like the little eddies or whirlwinds formed at the corner of streets. The whole vortex also travels, but its movement of translation is slow compared with its velocity of rotation.*

The properties of the atmosphere are much affected by the presence of watery vapour in it, which it acquires from contact with the surface of the sea, lakes, rivers and humid soil. The quantity which can rise into the air is limited by its temperature (page 77), and comes to be deposited again from various causes. The surface of the earth is cooled by radiation, and occasions the precipitation of dew from the air in contact with it. Vapour is also condensed into drops, from various agencies within the atmosphere itself. The following are the principal causes of clouds and rain. 1°. The ascent of air in the atmosphere, and its consequent rarefaction, which is attended with cold. A cloud will be observed within the receiver of an air-pump, on the plate of which a little water has been spilt, on

* See the work of Colonel Reid on the Law of Storms; and Athenæum, August 25, 1838, (p. 594.)

making two or three rapid strokes of the pump, which is due to this cause. It is observed in operation in the formation of the clouds and mists which settle on the summits of mountains. The wind passing over the surface of a level country is impeded by a mountain; rising in the atmosphere the stream overcomes the obstacle, and produces a cloud as it passes over the mountain, which appears stationary on its summit. 2°. The mixing of opposite currents of hot and cold air, both saturated with humidity, may occasion rain, from the circumstance, first conjectured by Dr. Hutton, that the currents of air on mixing and attaining a mean temperature, are incapable of sustaining the mean quantity of vapour. Thus, supposing equal volumes of air at 60° and 40°, both saturated with vapour, to be mixed; the tension of vapour at the former temperature being the 0.524th of an inch of mercury, and at the latter the 0.263rd of an inch, the mean tension is the 0.393rd of an inch. But the tension of vapour at 50°, the intermediate temperature is only the 0.375th of an inch; and consequently the excess of the former tension, or vapour of the 0.018th of an inch of tension, must condense as rain. But this is an inconsiderable cause of rain compared with the next. 3°. Contact of air in motion with the cold surface of the earth, appears to be the most usual cause of its refrigeration, and of the precipitation of rain from it. The mean temperature of January in this country is about 34°, but with a south-west wind the thermometer may be observed gradually to rise in the course of 48 hours to 54°. Now supposing this wind to be saturated with vapour at 54° and to be cooled to 34°, as it is on its first arrival, the moisture which it will deposit is very considerable, as will appear by the following calculation.

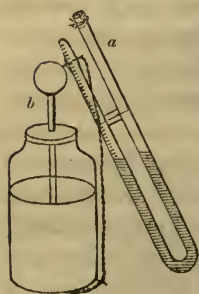
Tension of vapour at 54°	.	.	0.429 inch.
„ „ at 34°	.	.	0.214 „
<hr/>			
Condensed	.	.	0.215 „

When clouds form at temperatures below 32°, the aqueous vapour is converted into an infinity of little needle-like crystals, which often diverge from each other at angles of 60° and 120°, as do also the thin crystals in freezing water. Snow differs very much in the arrangement of these spiculæ, but the flakes are all

of the same configuration in the same storm. *Hail* is also produced by cold, but in circumstances which are entirely different. It occurs only in summer or in warm climates, and when the sun is above the horizon. It seems to be produced in a humid ascending current of air, greatly cooled by rarefaction, which has an upward velocity sufficient to sustain the falling hailstones at the same place till they attain considerable magnitude. The formation of hail is always attended with thunder or signs of electricity; and it has been found that small districts may be protected from its devastations by the elevation of many thunder rods.

Analysis of air.—A knowledge of the composition of the atmosphere followed that of its constituent gases. Various modes of analysis are practised:—1°. A stick of phosphorus introduced into a known measure of air in a graduated tube, effects a complete absorption of the oxygen in 24 hours. On afterwards withdrawing the phosphorus the diminution of volume may be observed, which always indicates 20 or 21 per cent of oxygen. 2°. A known measure of air may be mixed with a slight excess of hydrogen more than sufficient to combine with its oxygen, 100 volumes air, for example, with 50 volumes of hydrogen, and the mixture exploded in a strong glass tube of proper construction, by means of the electric spark. The diminution in volume of the gases after combustion is observed; and as oxygen and hydrogen unite in the exact ratio of one volume of the first to two volumes of the second, one-third of the diminution represents the volume of oxygen in the measure of air employed. The tube used for this purpose is called the voltaic eudiometer. The eudiometer of Dr. Ure is an excellent instrument of this kind. It is formed of a straight tube moderately stout, of about

FIG. 34.



1-4th or 3-8ths of an inch internal diameter, sealed at one end, and about 22 inches long. The closed end of this tube being softened by heat, two stout platinum wires are thrust through the glass from opposite sides of the tube, so that their extremities in the tube approach within one tenth of an inch of each other. These are intended for the transmission of the electric spark, and are retained, as if cemented, in the apertures of the glass when the latter cools. One half the tube next the

closed end is afterwards graduated into hundredths of a cubic inch, and the tube is bent in the middle, like a syphon, as represented by *a* in the figure. By a little dexterity, a portion of the gaseous mixture to be exploded is transferred to the sealed limb of the instrument, at the water or mercurial trough, and the measure noted with the liquid at the same height in both limbs. The mouth of the open limb may then be closed by a cork, which can be fixed down by soft copper wire. A chain being now hung to the one platinum wire, the other is presented to the prime conductor of an electric machine, or to the knob of a charged Leyden phial *b*, so as to take a spark through the mixture, which is thereby exploded. The risk of the tube being broken by the explosion, which is very considerable in the ordinary form of the eudiometer, is completely avoided in this instrument by the compression of the air retained by the cork in the open limb, this air acting as a recoil spring upon the occurrence of the explosion in the other limb.

3°. The combustion of the mixed gases may be determined without explosion by means of a little pellet of spongy platinum, and the experiment can then be conducted over mercury in an ordinary graduated tube.

4°. Another exact method of removing oxygen from air, recommended by Gay-Lussac, is the introduction into the air of slips of copper moistened with hydrochloric acid, which absorb oxygen with great avidity.

5°. Lastly, a method lately practised by Saussure; in which the air is deprived of its oxygen by agitating it with a small quantity of water and metallic lead in thin turnings, which becomes white hydrated oxide of lead. All these methods give accurate results when conducted with proper precautions. The conclusion which they have led to is, that the proportion of oxygen in 100 volumes of dry and pure air is not subject to variation, and lies between 20.8 and 21 volumes.* It is generally assumed as 21 volumes, which gives the proportions—

ATMOSPHERIC AIR BY WEIGHT.

Oxygen	23.1
Nitrogen	76.9
						<hr/>
						100.0

* Saussure, An. de Ch. et de Ph. t. 62, p. 219.

Besides these constituents, the atmosphere always contains a variable quantity of watery vapour and carbonic acid gas. The presence of the latter is observed by exposing to the air a bason of lime-water, which is soon covered by a pellicle of carbonate of lime. Its proportion is generally ascertained by adding barytes-water of a known strength, from a graduated pipette, to a large bottle of the air to be examined; agitating after each addition, till a slip of yellow turmeric paper is made permanently brown by the barytes-water after agitation, which proves that more of the latter has been added than is neutralized by the carbonic acid of the air. The carbonic acid is in the equivalent proportion (by weight) of the quantity of barytes which has been neutralized. Like every subject connected with the atmosphere, the proportion of carbonic acid which it contains has been ably investigated by the Saussures. The elder philosopher of that name detected the presence of this gas in the atmosphere resting upon the perpetual snows of the summit of Mont Blanc, so that there can be no doubt that carbonic acid is diffused through the whole mass of the atmosphere. The younger Saussure has ascertained, by a series of several hundred analyses of air that the mean proportion of carbonic acid is 4.9 volumes in 10,000 volumes of air, or almost exactly 1 in 2000 volumes; but it varies from 6.2 as a maximum to 3.7, as a minimum in 10,000 volumes. Its proportion near the surface of the earth is greater in summer than in winter, and during night than during day upon an average of many observations. It is also rather more abundant in elevated situations, as on the summits of high mountains, than in the plains; a distribution of this gas which proves that the action of vegetation at the surface of the earth is sufficient to keep down the proportion of it in the atmosphere, within a certain limit.* An enormous quantity of carbonic acid is discharged from the elevated cones of the active volcanoes of America, according to the observations of Bous-singault, which may partly account for the high proportion of that gas in the upper regions of the atmosphere. The gas emitted from the volcanoes of the old world, according to Davy and others, is principally nitrogen.

Carbonic acid is a constituent of the atmosphere which is essential to vegetable life, plants absorbing that gas, and all

* Saussure, *An. de Ch. et de Ph.* t. 38, p. 411, and t. 44, p. 5.

of them deriving from it a part, and some of them the whole of their carbon. Extensive forests, such as those of the Landes in France, which grow upon sands absolutely destitute of carbonaceous matter, derive their carbon entirely from this source. But the oxygen of the carbonic acid is not retained by the plant, for the lignin and other constituent principles of vegetables, contain, it is well known, no more oxygen than is sufficient to form water with their hydrogen, and which indeed has entered the plant as water. The oxygen of the carbonic acid must therefore be returned in some form to the atmosphere. The discharge of pure oxygen gas from the leaves of plants was first observed by Priestley, and the general action of plants upon the atmosphere has subsequently been minutely studied by Sir H. Davy and Dr. Daubeny. It appears that plants have a double action upon the atmosphere; they withdraw carbonic acid from it, appropriating the carbonaceous part of that gas to their own wants and evolving its oxygen; and they also absorb oxygen from the atmosphere and return carbonic acid in its place, an action corresponding with the respiration of animals. Of these actions the latter predominates during the night, and the former during the day, but the result of both is that plants during twenty-four hours yield considerably more oxygen than they consume. That they fully compensate for the loss of oxygen occasioned by the respiration of animals and other natural processes is not improbable. But the mass of the atmosphere is so vast that any change in its composition must be very slowly effected. It has indeed been estimated that the proportion of oxygen consumed by animated beings in a century does not exceed 1-7200th of the whole quantity.

Other gases and vaporous bodies are observed to enter the atmosphere, but none of them can afterwards be detected in it, with the exception perhaps of hydrogen in some form, probably as the light carburetted hydrogen of marshes, of which Boussingault believes that he has been able to detect the presence of an appreciable but exceedingly minute trace.* He observed concentrated sulphuric acid to be blackened when exposed in a glass capsule to the air, protected from dust, and at a distance from vegetation, which he ascribes to the occasional presence in the air of some volatile carbonaceous

* An. de Ch. et Ph. t. 57, p. 148.

compound, which is absorbed and decomposed by the acid. Of the odoriferous principles of plants, the miasmata of marshes and other matters of contagion, the presence, although sufficiently obvious to the sense of smell, or by their effects upon the human constitution, cannot be detected by chemical tests. But it may be remarked in regard to them, that few or none of the compound volatile bodies we perceive entering the atmosphere, could long escape destruction from oxidation. The atmosphere contains indeed within itself the means of its own purification, and slowly but certainly converts all organic substances exposed to it into simpler forms of matter, such as water, carbonic acid, nitric acid and ammonia. Although the occasional presence of matters of contagion in the atmosphere is not to be disputed, still it is an assumption without evidence, that these substances are volatile or truly vaporous. Other matters of infection with which we can compare them, such as the matter of cow-pox, may be dried in the air, and are not in the least degree volatile. Indeed volatility of a body implies a certain simplicity of constitution and limit to the number of atoms in its integrant particle, which true organic bodies appear not to possess. It is more probable that matters of contagion are highly organized particles of fixed matter, which may find its way into the atmosphere, notwithstanding, like the pollen of flowers, and remain for a time suspended in it; a condition which is consistent with the admitted difficulty of reaching and destroying those bodies by gaseous chlorine, and with the washing of walls and floors as an ordinary disinfecting practice. On this obscure subject I may refer to a valuable paper by the late Dr. Henry upon the application of heat to disinfection, in which it is proved that a temperature of 212° is destructive to such contagious matters as could be made the subject of experiment.*

The compounds of nitrogen with oxygen are the following :—

Nitrous oxide or protoxide of nitrogen	. . .	NO
Nitric oxide or deutoxide of nitrogen	. . .	NO ₂
Nitrous acid (hyponitrous acid of Turner)	. . .	NO ₃
Peroxide of nitrogen (nitrous acid of Turner, hyponitric acid of Thenard)	NO ₄
Nitric acid	NO ₅

* Phil. Mag. 2nd Series, v. 10, p. 363, and vol. 11, pp. 22, 207, (1832.)

NITROUS OXIDE.

Syn. PROTOXIDE OF AZOTE. *Eq.* 277 or 22.2; NO; density 1527.3; .

This gas was discovered by Dr. Priestley about 1776, and studied by Davy, whose "Researches, Chemical and Philosophical," published in 1809, contain an elaborate investigation of its properties and composition. Davy first observed the stimulating power of nitrous oxide when taken into the lungs, a property which has since attracted a considerable degree of popular attention to this gas.

Preparation. — Nitrous oxide is always prepared from the nitrate of ammonia. Some attention must be paid to the purity of that salt, which should contain no hydrochlorate of ammonia. It is formed by adding pounded carbonate of ammonia to pure nitric acid, which, if concentrated, may be previously diluted with half its bulk of water, so long as there is effervescence; and a small excess of the carbonate may be left at the end in the liquor. The solution is concentrated till its boiling point begins to rise above 250° , and a drop of it becomes solid on a cool glass plate. On cooling, it forms a solid cake, which may be broken into fragments. To obtain nitrous oxide, a quantity of this salt, which should never be less than 6 or 8 ounces, is introduced into a retort, or a globular flask, called a bolt-head

FIG. 35.



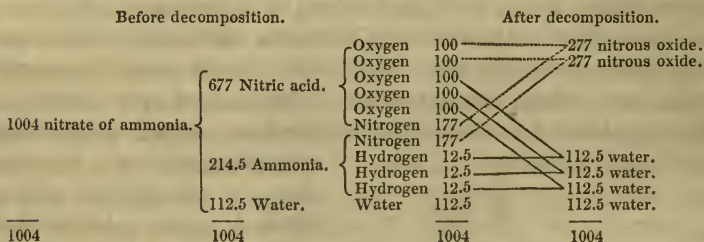
a, and heated by a charcoal choffer *b*, the diffused heat of which is more suitable than the heat of a lamp. Paper may be pasted over the cork of the bolt-head to keep it air-tight. At a temperature not under 340° the salt boils and begins to undergo decomposition, being resolved into nitrous oxide and water. As

heat is evolved in this decomposition, which is a kind of combustion or deflagration, the choffer must be withdrawn to such a distance from the flask, as to sustain only a moderate ebullition. If the temperature is allowed to rise too high, the ebullition becomes tumultuous, and the flask is

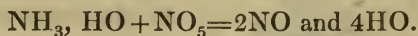
filled with white fumes, which have an irritating odour; and the gas which then comes off is little more than nitrogen. Nitrous oxide should be collected in a gasometer or in a gas-holder filled with water of a temperature about 90° , as cold water absorbs much of this gas. The whole salt undergoes the same decomposition, and nothing whatever is left in the retort.*

Nitrous oxide is likewise produced when the salt called nitro-sulphate of ammonia is thrown into an acid; and also when zinc and tin are dissolved in dilute nitric acid, but the latter processes do not afford the gas in a state of purity.

The nature of the decomposition of the nitrate of ammonia will be best explained by the following diagram, in which an equivalent of the salt, or 1004 parts, is supposed to be used. It will be observed that the three equivalents of hydrogen in the ammonia are burned, or combine with three equivalents of the oxygen of the nitric acid, and form water, while the two equivalents of nitrogen in the ammonia and nitric acid combine with the two remaining equivalents of the oxygen of the



Or in symbols :—



From the diagram it appears that 1004 grs. of the salt yield 554 grains of nitrous oxide and 450 grains of water. One grain of salt yields rather more than one cubic inch of gas.

Properties.—Nitrous oxide possesses the usual mechanical properties of gases, and has a faint agreeable smell. It has been liquefied by evolving it from the decomposition of the nitrate of ammonia in a sealed tube, and possessed in the liquid state

* For the preparation and properties of this and other gases, the *Elements of Chemistry* (1829) of the late Dr. Henry may be consulted with advantage.

an elastic force of above 50 atmospheres at 45°. The gas is formed by the union of a combining measure, or 2 volumes of nitrogen, with a combining measure, or 1 volume of oxygen, which are condensed into 2 volumes, the combining measure of this gas. The weight of a single volume, or the density of the gas, is therefore

$$\frac{976+976+1102.6}{2} = 1527.3$$


Cold water agitated with this gas dissolves about three-fourths of its volume of the gas, and acquires a sweetish taste, but, I believe, no stimulating properties. Bodies which burn in air, burn with increased brilliancy in this gas, if introduced in a state of ignition. A newly blown out taper with a red wick may be rekindled in it, as in oxygen. Mixed with an equal bulk of hydrogen and ignited by flame and the electric spark, it detonates violently. In all these cases of combustion, the nitrous oxide is decomposed, its oxygen uniting with the combustible and its nitrogen being set free. When transmitted through a red-hot porcelain tube, nitrous oxide is likewise decomposed and resolved into oxygen, nitrogen, and the peroxide of nitrogen.

Nitrous oxide was supposed by Davy to combine with alkalis, when generated in contact with them, but these compounds have since been found to contain nitrosulphuric acid.

This gas may be respired for two or three minutes without inconvenience, and when the gas is unmixed with air, and the lungs have been well emptied of air before respiring, it induces an agreeable state of revery or intoxication, often accompanied with considerable excitement, which lasts for a minute or two, and disappears without any unpleasant consequences. The gas from an ounce and a half or two ounces of nitrate of ammonia is sufficient for a dose, and it should be respired from a bag of the size of a large ox-bladder, and provided with a wooden tube of an inch internal diameter. The volume of the gas diminishes rapidly during the inspiration, and finally only a few cubic inches remain. An animal entirely confined in this gas soon dies from the prolonged effects of the intoxication.

NITRIC OXIDE.

Syn. DEUTOXIDE OF AZOTE, DEUTOXIDE OF NITROGEN, BINOXIDE OF NITROGEN (*Turner*,) NITROUS GAS (*Priestley*.)

Eq. 277 or 30.2; NO_2 ; density 1039.3; .

This gas which comes off during the action of nitric acid upon most metals, appears to have been collected by Dr. Hales, the father of pneumatic chemistry, but its properties were first minutely studied by Dr. Priestley.

Preparation.—Nitric oxide is easily procured by the action of nitric acid diluted to the specific gravity 1.2, upon sheet copper clipped into small pieces. As no heat is required, this gas may be evolved like hydrogen from a gas bottle (page 257.) Mercury may be substituted for copper, but it is then necessary to apply a gentle heat to the materials. This gas may be collected and retained over water without loss.

In dissolving in nitric acid, the copper takes oxygen from one portion of acid and becomes oxide of copper, which combines with another portion of acid, and forms the nitrate of copper, the solution of which is of a blue colour. The portion of nitric acid which is decomposed, losing three equivalents of oxygen and retaining two, appears as nitric oxide gas. This is more clearly shown in the following diagram :—

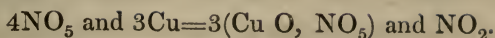
ACTION OF NITRIC ACID UPON COPPER.

Before decomposition.

After decomposition.

677 Nitric acid	{	Nitrogen . 177	377 Nitric oxide.
		Oxygen . 100	
		Oxygen . 100	
		Oxygen . 100	
		Oxygen . 100	
		Oxygen . 100	
396 Copper .		Copper . 396	
677 Nitric acid		Nitric acid 677	1173 Nitrate of copper.
396 Copper .		Copper . 396	
677 Nitric acid		Nitric acid 677	1173 Nitrate of copper.
396 Copper .		Copper . 396	
677 Nitric acid		Nitric acid 677	1173 Nitrate of copper.
3896		3896	3896

Or in symbols :—



Properties.—This gas is colourless, but when mixed with air it produces ruddy fumes of the peroxide of nitrogen. It is irritating, and causes the glottis to contract spasmodically when an attempt is made to respire it. Nitric oxide has never been liquefied: water at 60° according to Dr. Henry, takes up only 5 or 6 per cent of this gas. It is formed of one combining measure of nitrogen or 2 volumes, and two combining measures of oxygen or 2 volumes, united without condensation, so that the combining measure of nitric oxide contains 4 volumes. The weight of one volume, or the density of the gas, is therefore

$$\frac{976+976+1102.6+1102.6}{4} = 1039.3.$$

This gas is not decomposed by a low red heat.

Many combustibles do not burn in nitric oxide, although it contains half its volume of oxygen. A lighted candle and burning sulphur are extinguished by it; mixed with hydrogen, it is not exploded by the electric spark or by flame, but it imparts a green colour to the flame of hydrogen burning in air. Phosphorus and charcoal, however, introduced in a state of ignition into this gas, continue to burn with increased vehemence. The state of combination of the oxygen in this gas appears to prevent that substance from uniting with combustibles, unless, like the two last mentioned, they evolve so much heat as to decompose the nitric oxide. Several of the more oxidable metals, such as iron, withdraw the half of the oxygen from this gas, when left in contact with it, and convert it into nitrous oxide.

No property of nitric oxide is more remarkable than its attraction for oxygen, and it may be employed to separate this from all other gases. Nitric oxide indicates the presence of free oxygen in a gaseous mixture, by the appearance of fumes which are pale and yellow, with a small, and reddish brown and dense with a large proportion of the latter gas; and also by a subsequent contraction of the gaseous volume, arising from the absorption of these fumes by water. Added in sufficient quantity, nitric oxide will thus withdraw oxygen most

completely from any mixture. But notwithstanding this property, nitric oxide cannot be employed with advantage in the analysis of air or similar mixtures, for the contraction which it occasions does not afford certain data for determining the proportion of oxygen which has disappeared. Nitric oxide is capable of combining with different proportions of oxygen, a combining measure or 4 volumes of the gas uniting, in such experiments, with 1, 2 or 3 volumes of oxygen, and forming nitrous acid, peroxide of nitrogen or nitric acid, or several of these compounds at the same time.

This oxide of nitrogen, like the preceding, is a neutral body, and has a very limited range of affinity. A substance is left on igniting the nitrate of potash or barytes, which was supposed to be a compound of nitric oxide with potassium, or barium, but Mitscherlich finds it to be either the caustic protoxide itself or the peroxide of the metal. But nitric oxide is absorbed by a solution of the sulphate of iron, which it causes to become black; the greater part of the gas may be expelled again by boiling the solution. All the soluble proto-salts of iron have the same property, and the nitric oxide remains attached to the oxide of iron when precipitated in the insoluble salts of that metal. The proportion of nitric oxide in these combinations is found by Peligot to be definite; one eq. of the nitric oxide to four of the protoxide of iron; or, the nitric oxide contains the proportion of oxygen required to convert the protoxide into peroxide of iron.* Nitric oxide is also absorbed by nitric acid. With sulphurous acid nitric oxide forms a compound which will be more particularly noticed under that acid.

NITROUS ACID.

Syn. AZOTOUS ACID (Thenard,) HYPONITROUS ACID (Turner.)
Eq. 477 or 38.2; NO_3 .

The direct mode of forming this compound is by mixing 4 volumes of nitric oxide with 1 volume of oxygen, both perfectly dry, and exposing the mixture to a great degree of cold. The gases unite and condense into a liquid of a green colour, which is very volatile, and forms a deep reddish yellow coloured

* An. de Ch. et de Ph. t. 54, p. 17.

vapour. Nitrous acid prepared in this way is decomposed at once when thrown into water; an effervescence occurring from the escape of nitric oxide, and nitric acid being produced which gives stability to a portion of the nitrous acid. Nitrous acid cannot be made to unite directly with alkalies and earths, probably owing to the action of water first described. But when oxygen gas is mixed with a large excess of nitric oxide, in contact with a solution of caustic potash, the gases were found by Gay-Lussac always to disappear in the proportions of nitrous acid, which was produced and entered into combination with the potash, forming a *nitrite* of potash. Similar nitrites may also be produced by calcining the nitrate of potash till the fused salt becomes alkaline; or by boiling the nitrate of lead with metallic lead. The nitrite of potash may be dissolved and filtered, and the solution precipitated by nitrate of silver; a process which gives the nitrite of silver, a salt possessing a sparing degree of solubility like that of cream of tartar, but which may be purified by solution and crystallization, and then affords a ready means of obtaining the other nitrites by double decomposition (Mitscherlich.) When free sulphuric acid is added to a solution of nitrite of silver, the liberated nitrous acid is immediately resolved into nitric acid and nitric oxide. The subnitrite of lead, on the other hand, may be decomposed by the bisulphate of potash or soda to obtain a neutral nitrite of one of these bases (Berzelius.)

Nitrous acid is also capable of combining with several acids, in particular with iodic, nitric, and sulphuric acids. Its combination with the last is a crystalline solid of specific gravity 1.831, which is of considerable interest from its occurrence in the manufacture of sulphuric acid. According to the analysis of Gaultier de Claubry, its constituents are 5 eq. of sulphuric acid, 2 of nitrous acid and 4 of water. When moist sulphurous acid gas and peroxide of nitrogen are in contact, this crystalline compound is formed, the sulphurous acid gaining the oxygen which the other loses. A little nitrogen appears at the same time, so that a portion of the peroxide of nitrogen must be completely decomposed. If the crystalline compound comes in contact with steam or a small quantity of water, the sulphuric acid combines exclusively with the water, and the liberated nitrous acid is resolved into nitric oxide and peroxide of nitrogen, both of which escape as gas. But with a large quantity of water a por-

tion of the nitrous acid is always decomposed into nitric oxide gas and nitric acid.*

It must be admitted that some obscurity still hangs over the nature of this acid, when uncombined, the formation of the nitrites by Gay-Lussac's process appearing to be incompatible with the properties ascribed to the free acid by Dulong. Its tendency to combine with acids has already been noticed as assimilating this compound of nitrogen to arsenious acid and the oxide of antimony (page 146.)

PEROXIDE OF NITROGEN.

Syn. NITROUS ACID (*Turner*,) HYPONITRIC ACID, NITROUS GAS (*Berzelius*.) *Eq.* 577 or 46.2; NO_4 ; density 3181.2; .

This compound forms the principal part of the ruddy fumes which always appear on mixing nitric oxide with air. As it cannot be made to unite either directly or indirectly with bases, and has no acid properties, any designation for this oxide of nitrogen which implies acidity should be avoided, and the name nitrous acid in particular, which is applied on the continent to the preceding compound. The name peroxide of nitrogen is more in accordance with the rules generally followed in naming such compounds.

Preparation. — When 4 volumes of nitric oxide and 2 of oxygen, both perfectly dry, are mixed, this compound is alone produced, and the 6 volumes of mixed gases are condensed into 2 volumes, which may be considered the combining measure of peroxide of nitrogen. The weight of 1 volume, or the density of this gas must therefore be

$$\frac{1039. \times 34 + 1102.6 \times 2}{2} = 3181.2.$$

The peroxide of nitrogen is also contained in the coloured and fuming nitric acid of commerce, and may be obtained in the liquid condition, by gently warming that acid, and condensing the vapour which comes over, by transmitting it through a glass tube surrounded by ice and salt. But it is prepared with most advantage from the nitrate of lead, the crystals of which, after being pounded and dried, are distilled in a retort of stoneware

* An. de Ch. et de Ph. t. 45, p. 284.

or hard glass, at a red heat, and the red vapours condensed in a receiver kept very cold by a freezing mixture. Oxygen gas escapes during the whole process, the nitric acid of the nitrate of lead being resolved into oxygen and peroxide of nitrogen; or $\text{NO}_5 = \text{NO}_4$ and O. As obtained by the last process, which was proposed by Dulong, peroxide of nitrogen is a highly volatile liquid, boiling at 82° , of a red colour at the usual temperature, orange yellow at a lower temperature, and nearly colourless below zero, of density 1.451, and a white solid mass at -40° . It is exceedingly corrosive, and like nitric acid stains the skin yellow. The red colour of its vapour becomes paler at a low temperature, but with heat increases greatly in intensity, so as to appear quite opaque when in a considerable body at a high temperature. It is the vapour which Brewster observed to produce so many dark lines in the spectrum of a ray of light which had passed through it (page 92.) The peroxide is not decomposed by a low red heat, and appears to be the most stable of the oxides of nitrogen. No compound of it is known, unless peroxide of nitrogen be the radical, as some suppose, of nitric acid. But Berzelius is inclined to consider this oxide as itself a compound of nitric and nitrous acids, for $\text{NO}_5 + \text{NO}_3 = 2\text{NO}_4$.*

The liquid peroxide of nitrogen is partially decomposed by water, nitric oxide coming off with effervescence, and more and more nitric acid being produced, in proportion to the quantity of water added; but a portion of the peroxide always escapes this action, being protected by the nitric acid formed. In the progress of this dilution the liquid undergoes several changes of colour, passing from red to yellow, from that to green, then to blue, and becoming at last colourless. The peroxide of nitrogen is readily decomposed by the more oxidable metals, and is a powerful oxidizing agent.

NITRIC ACID.

Syn. AZOTIC ACID (Thenard.) Eq. 677; NO_5 ; does not exist except in combination.

A knowledge of this highly important acid has descended from the earliest ages of chemistry, but its composition was first

* *Traité de Chimie*, par J. J. Berzelius, traduit par B. Valerius, Bruxelles, 1838, t. 1, p. 195. An excellent edition of the most valuable system of chemistry which we at present possess.

ascertained by Cavendish, in 1785. He succeeded in forming nitric acid from its elements, by transmitting a succession of electric sparks during several days, through a small quantity of air, or through a mixture of 1 volume of nitrogen and $2\frac{1}{2}$ volumes of oxygen, confined in a small tube over water, or over solution of potash; in the last case the absorption of the gases was complete and nitrate of potash was obtained. A trace of this acid in combination with ammonia has been detected in the rain of thunder storms, produced probably in the same manner. It was also observed by Gay-Lussac to be the sole product when nitric oxide is added, in a gradual manner to oxygen in excess over water; the gases then unite and disappear in the proportion of 4 volumes of the former to 3 of the latter. It is also a constituent of the salt, nitre or saltpetre, found in the soil of India and Spain, which is a nitrate of potash, and also of nitrate of soda which occurs in large quantities in South America.

Preparation.—This acid cannot exist in an insulated state, but is always in combination with water, as in aqua fortis or the hydrate of nitric acid, or with a fixed base, as in the ordinary nitrates. The hydrate, (which is popularly termed nitric acid,) is eliminated from nitrate of potash by means of oil of vitriol, which is itself a hydrate of sulphuric acid. That acid unites with potash, in this decomposition, and forms sulphate of potash, displacing nitric acid, which last brings off in combination with itself the water of the oil of vitriol. There is a great advantage, first pointed out by Mr. Phillips, in using two equivalents of oil of vitriol to one of nitrate of potash, which is 97 of the former to 100 of the latter, or nearly equal weights. The acid and salt, in these proportions, are introduced into a capacious plain retort, provided with a flask as a receiver. Upon the application of heat, a little of the nitric acid first evolved undergoes decomposition, and red fumes appear, but soon the vapours become nearly colourless, and are easily condensed in the receiver. During the whole distillation, the temperature need not exceed 260° . The mass remains pasty till all the nitric acid is disengaged, and then enters into fusion; red vapours again appearing towards the end of the process. If the neck of the retort now be heated, the residuary salt, while still fluid, may be poured out into a bason; it is the bisulphate of potash, which may be used for different purposes after it has solidified. The rationale of this important process is exhibited in the following diagram :—

PROCESS FOR NITRIC ACID.

Before decomposition.		After decomposition.	
1267	Nitrate of potash.	789.5	Nitric acid and water.
	{ Nitric acid . 677		
	{ Potash . . 590		
613.5	Oil of vitriol.		
	{ Water . . 112.5		
613.5	Oil of vitriol.	1091	Sulphate of potash } bisul. of
	{ Sulphuric acid 501	613.5	Sulphate of water. } potash.
	{ Oil of vitriol . 613.5		
2494		2494	

In this operation twice as much sulphuric acid is employed, as is required to neutralize the potash of the nitre, by which means the whole nitric acid is eliminated without loss at a moderate temperature, and a residuary salt is left which is easily removed from the retort.

With half the preceding quantity, or a single equivalent of oil of vitriol, the materials in the retort are apt to undergo a vesicular swelling, upon the application of heat, and to pass into the receiver. Abundance of ruddy fumes are also evolved, that are not easily condensed, and prove that the nitric acid is decomposed. The temperature in this process must also be raised inconveniently high towards the end of the operation, in order to decompose the whole nitre. The peculiarities of the decomposition here arise from the formation of bisulphate of potash in the operation, the whole sulphuric acid uniting in the first instance with half the potash of the nitre. Now, it is only at an elevated temperature that the acid salt thus formed can decompose the remaining nitre; a temperature which is sufficient to decompose nitric acid, as may be proved by transmitting the vapour of the concentrated acid through a tube heated to the same degree.

Properties.—The acid prepared by the first process is colourless or has only a straw yellow tint. If the oil of vitriol has been in its most concentrated condition, which is seldom the case, the nitric acid is in its state of highest concentration also, and contains no more than a single equivalent of water, according to Mitscherlich. The density of this acid is 1.522 at 58°; but a slight heat disengages a little peroxide of nitrogen from it, and its density becomes 1.521. It boils at 187°, but when distilled, it is partially decomposed by the heat and affords a product of a strong yellow colour. Its vapour transmitted through a porcelain tube, heated to dull redness, is decomposed in a great measure into oxygen and peroxide of nitrogen; and into oxygen and nitrogen gases, when the tube is heated to white-

ness. The colourless liquid acid becomes yellow, when exposed to the rays of the sun, and on loosening the stopper of the bottle, it is sometimes projected with force, from the state of compression of the disengaged oxygen. Hence to preserve this acid colourless it must be kept in a covered bottle. It congeals at about -40° , but diluted with half its weight of water, it becomes solid at $1\frac{1}{2}^{\circ}$, and with a little more water its freezing point is again lowered to -45° . Exposed to the air the concentrated acid fumes, from the condensation by its vapour of the moisture in the atmosphere. It also attracts moisture from damp air, and increases in weight; and when suddenly mixed with 3-4ths of its weight of water, may rise in temperature from 60° to 140° .

Nitric acid has a great affinity for water, and diminishes in density with the proportion of water added to it. A table has been constructed by Dr. Ure, in which the per centage of absolute acid is expressed in mixtures of various densities, which is useful for reference and will be given in an appendix. There are several definite hydrates of this acid. The most concentrated acid contains a single equivalent of water; a second acid appears to exist, having a density of about 1.48, which contains two of water, and forms the nitric acid which has little or no action upon tin, iron and some other metals; there is still a third acid of density 1.42, which contains four equivalents of water. This last hydrate was found by Dr. Dalton to have the highest boiling point of any hydrate of nitric acid, namely 248° , and both weaker and stronger acids are brought to this strength by continued ebullition, the former losing water and the latter acid. The density of the vapour of this hydrate is found to be 1243 by A. Bineau, and it contains 2 volumes of nitrogen, 5 volumes of oxygen and 8 volumes of steam condensed into 10 volumes, which are therefore the combining measure of this vapour.*

Nitric acid is exceedingly corrosive, and one of the strongest acids, yielding only in that respect to sulphuric acid. The facility with which it parts with its oxygen, renders it very proper for oxidating bodies in the humid way, a purpose for which it is constantly employed. Nearly all the metals are oxidized by means of it; some of them with extreme violence, such as copper, mercury and zinc, when the concentrated acid is used; and

* An. de Ch. et de Ph. t. 68, p. 418.

tin and iron by the acid very slightly diluted. Poured upon red hot charcoal, it causes a brilliant combustion. When mixed with a fourth of its bulk of sulphuric acid, and thrown upon a few drops of oil of turpentine, it occasions an explosive combustion of the oil. Sulphur digested in nitric acid at the boiling point is raised to its highest degree of oxidation and becomes sulphuric acid; iodine is also converted by it into iodic acid. Most vegetable and animal substances are converted by dilute nitric acid into oxalic, malic and carbonic acids. It stains the cuticle and nails of a yellow colour, and has the same effect upon wool; the orange patterns upon woollen table covers are produced by means of it. In the undiluted state it forms a powerful cautery.

In acting upon the less oxidable metals, such as copper and mercury, nitric acid is itself decomposed, and nitric oxide gas produced, which comes off with effervescence. Palladium and silver when they are dissolved by the acid in the cold, produce nitrous acid in the liquor and evolve no gas, but this is very unusual in the solution of metals by nitric acid. Those metals, such as zinc, which are dissolved in diluted acids with the evolution of hydrogen, act in two ways upon nitric acid; sometimes they decompose it, so as to disengage a mixture of peroxide of nitrogen and nitric oxide, and at other times they decompose both water and nitric acid at once, in such proportions that the hydrogen of the water combines with the nitrogen of the acid to form ammonia, which last combines with another portion of acid, and is retained in the liquor as nitrate of ammonia. The protoxide of nitrogen is also evolved when zinc is dissolved in very feeble nitric acid, which may arise from the action of hydrogen upon nitric oxide. Nitric acid, in its highest state of concentration, exerts no violent action upon certain organic substances, such as lignin or woody fibre and starch, for a short time, but unites with them and forms singular compounds. A proper acid for such experiments is procured with most certainty by distilling 100 parts of nitre, with no more than 60 parts of the strongest oil of vitriol. If paper is soaked for one minute in such an acid, and afterwards washed with water, it is found to shrivel up a little and become nearly as tough as parchment, and when dried to be remarkably inflammable, catching fire at so low a temperature as 356° , and burning without any nitrous odour. (Pelouze.)

Nitric acid forms an important class of salts, the nitrates, which occasion deflagration when fused with a combustible at a high temperature, from the oxygen in their acid, and are remarkable as a class for their general solubility, no nitrate being insoluble in water. The nitrate of the black oxide of mercury is perhaps the best soluble of these salts. In neutral nitrates the oxygen in the acid is always five times that in the base. The nitrates of potash, soda, ammonia, barytes and strontian, are anhydrous; but the nitrates of the extensive magnesian class of oxides all contain water in a state of intimate combination, one equivalent at least of it appearing to be inseparable from the salt, and they have a formula analogous to that of hydrated nitric acid, or the nitrate of water itself. The nitric acid of sp. gr. 1.42 appears to be the proper nitrate of water, and of the four atoms of water which it contains, one is combined with the acid as base, and may be named *basic* water, while the other three are in combination with the nitrate of water, and may be termed the *constitutional* water of that salt. The same three atoms of constitutional water are found in all the magnesian nitrates, with the addition often of another three atoms of water, as appears from the following formulæ:—

Nitric acid, 1.42.	. . .	HO, NO ₅ + 3HO
Prismatic nitrate of copper.	. . .	CuO, NO ₅ + 3HO
Rhomboidal nitrate of copper.	. . .	CuO, NO ₅ + 3HO + 3HO
Nitrate of magnesia.	. . .	MgO, NO ₅ + 3HO + 3HO

The proportion of water in the nitrate of magnesia may be reduced, by heating the salt, to one atom, leaving the compound MgO, NO₅ + HO; but on urging the temperature still higher, the last atom of water and the acid are expelled together, and magnesia is left behind, neither this nor any other nitrate of the magnesian class being capable of existing without an atom of water. The nitrates of the potash and magnesian classes do not combine together, and no double nitrates are known, nor nitrates with excess of acid. The nitrates with excess of metallic oxide, which are called subnitrates, appear to be formed on the type of the magnesian class: the subnitrate of copper, being HO, NO₅ + 3CuO, or nitrate of water with three atoms of constitutional oxide of copper; while the nitrate of red oxide of mercury is HgO, NO₅ + HgO, or it resembles the nitrate of magnesia which has been strongly dried, MgO, NO₅ + HO. (Kane.)

Nitric acid in a solution cannot be detected by precipitating that acid in combination with any base, as the nitrates are all soluble, so that tests of another nature must be had recourse to, to ascertain its presence. A highly diluted solution of sulphate of indigo may be boiled without change, but on adding to it at the boiling temperature, a liquid containing free nitric acid, the blue colour of the indigo is instantly destroyed. If it is a neutral nitrate which is tested, a little sulphuric acid should be added to the solution, to liberate the nitric acid, before mixing it with the sulphate of indigo. It is also necessary to guard against the presence of a trace of nitric acid in the sulphuric acid. Another test of the presence of nitric acid has lately been proposed by de Richemont. The liquid containing the nitrate is mixed with rather more than an equal bulk of oil of vitriol, and when the mixture has become cool, a few drops of a strong solution of protosulphate of iron are added to it. Nitric oxide is evolved, and combines with the protosulphate of iron, producing a rose or purple tint even when the quantity of nitric acid is very small. One part of nitric acid in 24,000 of water has been detected in this manner. Free nitric acid also is incapable of dissolving gold-leaf, although heated upon it, but acquires that property when a drop of hydrochloric acid is added to it. But in testing the presence of this acid, it is always advisable to neutralize a portion of the liquor with potash, and to evaporate so as to obtain the thin prismatic crystals of nitre, which may be recognized by their form, by their cooling nitrous taste, their power to deflagrate combustibles at a red heat, and by the characteristic action of the acid they contain, when liberated by sulphuric acid, upon copper and other metals, in which ruddy nitrous fumes are produced. If nitric acid be rigidly pure, it may be diluted with distilled water, and is not disturbed by nitrate of silver, nor by chloride of barium; the first of which detects the presence of hydrochloric acid by producing a white precipitate of chloride of silver; the last detects sulphuric acid by forming the white insoluble sulphate of barytes. The fuming nitric acid may be freed from hydrochloric acid, by retaining it warm on a sand-bath for a day or two, when the chlorine of the hydrochloric acid goes off as gas. To free it from sulphuric, it should be diluted with a little water, and distilled from nitrate of barytes; but the process for

nitric acid which has been described gives it without a trace of sulphuric acid, when carefully conducted.

Uses. Nitric acid is sometimes used in the fumigations required for contagious diseases, particularly in wards of hospitals from which the patients are not removed, the fumes of this acid being greatly less irritating than those of chlorine. For the purpose of fumigation pounded nitre and concentrated sulphuric acid are used, being heated together in a cup. Nitric acid is par excellence the solvent of metals, and has other most numerous and varied applications not only in chemistry, but likewise in the arts and manufactures.

SECTION IV.

CARBON.

Eq. 76.44 or 6.13; (75.6 or 6.05, *Dr. Clark*,) C; *density of vapour (hypothetical)* 421.5.

Carbon is found in great abundance in the mineral kingdom united with other substances, as in coal of which it is the basis, and in the acid of carbonates; it is also the most considerable element of the solid parts in both animals and vegetables. It exists in nature or may be obtained by art, under a variety of appearances, and possessed of very different physical properties. Carbon is a dimorphous body, occurring crystallized in the diamond and graphite in wholly different forms, and when artificially produced forming several amorphous varieties of charcoal which are very unlike each other.

Diamond.—This valuable gem is found throughout the range of the Ghauts in India, but chiefly at Golconda, in Borneo and also in Brazil. It is always associated with transported materials, such as rolled gravel, and has never been found in situ, so that its origin is doubtful, although it is now generally supposed to have been produced by the slow decomposition of vegetable matter. On removing the crust with which the crystals are covered, they are exceedingly brilliant, refract light powerfully, and are generally perfectly transparent, although diamonds are sometimes black, blue and of a beautiful rose-colour. The primitive form of diamond is the regular octohedron, or two four-sided pyramids, of which the faces are equilateral triangles, applied base to base. It is also often found in

figures bounded by 48 curved triangular faces, but can always be cleaved in the direction of the faces of the octohedron, which possess that particular brilliancy characteristic of the diamond. The diamond is the hardest of the gems. An edge of its crystal formed by flat planes only scratches glass, but if the edge is formed of curved faces, like the edge of a convex lens, it then, besides abrading the surface, produces a fissure to a small depth, and in the form of the glazier's diamond is used to cut glass. The diamond is remarkably indestructible, and may be heated to whiteness in a covered crucible without injury, but it begins to burn in the open air, at about the melting point of silver, charcoal sometimes appearing on its surface, and is entirely converted into carbonic acid gas. It is more quickly consumed in fused nitre, when the carbonic acid is retained by the potash; this is a simple mode of analyzing the diamond, by which it has been proved to be perfectly pure carbon. The diamond is a non-conductor of electricity. Its density varies from 3.5 to 3.55.

Graphite.—This mineral, which is also known as black lead and plumbago, occurs in rounded masses deposited in beds in the primitive formations, particularly in granite, micaschist and primitive limestone. Borrowdale in Cumberland is a celebrated locality of graphite, and affords the only specimens which are sufficiently hard for making pencils. It is occasionally found crystallized in plates which are six-sided tables. Graphite may also be produced artificially, by putting an excess of charcoal in contact with fused cast iron, when a portion of the carbon dissolves, and separates again on cooling, in the form of large and beautiful crystalline leaflets. In the condition of graphite, carbon is perfectly opaque, soft to the touch, possessed of the metallic lustre, and of a specific gravity about 2.5. It always contains a small quantity of iron, often amounting to 5 per cent, but in some specimens, as in those from Barreros in Brazil, not more than a trace, which is to be considered an accidental constituent, and not essential to the mineral. Neither in the form of diamond nor graphite does carbon exhibit any indication of fusion or volatility under the most intense heat. *Anthracite* is nearly pure carbon, but always contains a portion of hydrogen, and is more analogous to coal than to graphite.

Charcoal.—Owing to its infusibility carbon presents itself under a variety of aspects, according to the structure of the

substance from which it is derived, and the accidental circumstances of its preparation. The following are the principal varieties: gas-carbon, lamp black, wood charcoal, coke, and ivory black.

1°. Gas-carbon has the metallic lustre, and a density of 1.76; it is compact, generally of a mammillated structure, but sometimes in fine fibres, and considerably resembles graphite, but is too hard to give a streak upon paper. It is the product of a slow deposition of carbon from coal gas at a high temperature and is frequently found to line the gas retorts to a considerable thickness, and to fill up accidental fissures in them.*

2°. Lamp black is the soot of imperfectly burned combustibles such as tar or resin. Carbon is deposited in a powder of the same nature, when alcohol vapour or a volatile oil is transmitted through a porcelain tube at a red heat; and the lustrous charcoal which is obtained on calcining starch, sugar and many other organic substances, which fuse and afford a bright vesicular carbon of a metallic lustre, is possessed of the same characters. It is deficient in an attraction for organic matters in solution, which ordinary charcoal possesses.

3°. Wood charcoal. Wood was found by Karsten to lose 57 per cent of its weight when thoroughly dried at 212° and 10 per cent more at 304°. The remaining 33 parts of baked wood afforded, when calcined, 25 of charcoal, while 100 parts of the same wood calcined, without being previously dried, left only 14 per cent of carbon. It is the absence of this large quantity of water which causes the heat of burning charcoal to be so much more intense than that of wood. When calcined at a high temperature, charcoal becomes dense, hard and less inflammable. The knots in wood sometimes afford a charcoal which is particularly hard, and is used in polishing metals, but it contains silica. From the minuteness of its pores, the charcoal of wood absorbs many times its volume of the more liquefiable gases, such as ammoniacal gas, hydrochloric acid, sulphuretted hydrogen and carbonic acid, condensing 35 volumes of the last. It also absorbs moisture with avidity from the atmosphere, and other condensible vapours, such as odoriferous effluvia. From this last property freshly calcined charcoal, when wrapt up in clothes which have contracted a disagreeable odour,

* Dr. Colquhoun, *Annals of Philosophy*, New Series, vol. 12, p. 1.

destroys it, and has a considerable effect in retarding the putrefaction of organic matter with which it is placed in contact. Water is also found to remain sweet, and wine to be improved in quality if kept in casks of which the inside has been charred. In the state of a coarse powder wood charcoal is particularly applicable as a filter for spirits, which it deprives of the essential oil which they contain. It is much less destructible by atmospheric agencies than wood, and hence the points of stakes are often charred, before being driven into the ground, in order to preserve them.

4°. The coke of those species of coal, which do not fuse when heated, is a remarkably dense charcoal, considerably resembling that of wood, and of great value as fuel from the high temperature which can be produced by its combustion. When burned it generally leaves 2 or 3 per cent of earthy ashes, while the ashes from wood charcoal seldom exceed 1 per cent.

5°. Ivory black, bone-charcoal and animal charcoal are names applied to bones calcined or converted into charcoal in a close vessel. The charcoal thus produced is mixed with not less than 10 times its weight of phosphate of lime, and being in a state of extreme division, exposes a great deal of surface. It possesses a remarkable attraction for organic colouring matters, and is extensively used in withdrawing the colouring matter from syrup, in the refining of sugar, from the solution of tartaric acid, and in the purification of many other organic liquors. The usual practice, which was introduced by Dumont, is to filter the liquid to be discoloured, through a bed of this charcoal, in grains of the size of those of gunpowder, and of two or three feet in thickness. It is found that the discolouring power is greatly reduced by dissolving out the phosphate of lime from ivory black by an acid, although this must be done in certain applications of it, as when it is used to discolour the vegetable acids. A charcoal possessed of the same valuable property even in a higher degree for its weight, is produced by calcining dried blood, horns, hoofs, clippings of hides, in contact with carbonate of potash, and washing the calcined mass afterwards with water. Even vegetable matters afford a charcoal, possessed of considerable discolouring power, if mixed with chalk, calcined flint or any other earthy powder, before being carbonized. One hundred parts of pipe clay made into a thin

paste with water, and well mixed with 20 parts of tar and 500 of coal finely pulverized, have been found to afford, after the mass was dried and ignited out of contact with air, a charcoal which was little inferior to bone-black in quality. When charcoal which has been once used in such a filter, is calcined again, it is found to possess very little discolouring power. This is owing to the deposition upon its surface of a lustrous charcoal, of the lamp black variety, produced by the decomposition of the organic colouring matters, which has little or no discolouring power. But if the charcoal of the sugar filters be allowed to ferment, the foreign matter in it is destroyed; and if afterwards well washed with water and dried, before being calcined, it will be found to recover a considerable portion of its original discolouring power.

Bussy has constructed, from observation, the following table of the efficiency of the different charcoals. These substances are compared with ivory black, as being the most feeble species, although this is superior by several degrees to the best wood charcoal. The relative efficiency, it will be observed, is not the same for two different kinds of colouring matter :

Species of Charcoal same weight.	Relative Deco- ration of sul- phate of indigo.	Relative Deco- ration of Syrup.
Blood charred with carbonate of potash . . .	50	20
Blood charred with chalk	18	11
Blood charred with phosphate of lime . . .	12	10
Glue charred with carbonate of potash . . .	36	15.5
White of egg charred with the same. . . .	34	15.5
Gluten charred with the same.	10.6	8.8
Charcoal from acetate of potash	5.6	4.4
Charcoal from acetate of soda.	12	8.8
Lamp black, not calcined	4	3.3
Lamp black calcined with carbonate of potash. .	15.2	10.6
Bone charcoal, after the extraction of the earth of bones by an acid, and calcination with po- tash.	45	20
Bone charcoal treated with an acid.	1.87	1.6
Oil charred with the phosphate of lime. . .	2	1.9
Bone charcoal, in its ordinary state. . . .	1	1

This remarkable action of charcoal in withdrawing matters from solution is certainly an attraction of surface, but it is capable notwithstanding, of overcoming chemical affinities of some intensity. The matters remain attached to the surface of the charcoal, without being decomposed or altered in nature, For if the blue sulphate of indigo be neutralized and then fil-

tered through charcoal, the whole colouring matter is retained by the latter, and the filtered liquid is colourless. But a solution of caustic alkali will divest the charcoal of the blue colouring matter, and carry it away in solution. Other substances also are carried down by animal charcoal, besides animal matters. Lime from lime water, iodine from solution in iodide of potassium, soluble subsalts of lead, and metallic oxides dissolved in ammonia and caustic potash; but it has little or no action upon most neutral salts. The charcoal is apt with time to react upon the substance it carries down, probably from their closeness of contact, reducing the oxide of lead, for instance, in a short time to the metallic state.

Carbon is chemically the same under all these forms. This element cannot be crystallized artificially by the usual methods of fusion, solution or sublimation, if we except its solution in cast iron, which gives it in the form of graphite and not of the diamond. It is chemically indifferent to most bodies at a low temperature, but combines directly with some metals by fusion and forms *carburets*. When heated to low redness it burns readily in air or oxygen, forming a gaseous compound carbonic acid, which when cool has exactly the bulk of the original oxygen. With half the proportion of oxygen in carbonic acid, carbon forms a protoxide, carbonic oxide gas. This gas being supposed similar to steam or to nitrous oxide in its constitution, will be composed of 2 vols. of carbon vapour and 1 vol. of oxygen gas condensed into 2 volumes, an assumption upon which the density of carbon vapour, which there are no means of determining experimentally, is usually calculated, and made about 421.5; the combining measure of this vapour containing 2 volumes (page 132.) It has been inferred from the results of recent organic analysis, that the number 76.44, fixed upon by Berzelius as the equivalent of carbon is too high, and that 75.6 is near the truth.*

Uses.—Several valuable applications of this substance have already been incidentally described. Carbon may be said to surpass all other bodies whatever in its affinity for oxygen at a high temperature; and being infusible, easily got rid of by combustion, and forming compounds with oxygen which escape

* By Dr. Clark; see also Dumas; Phil. Mag. 3rd. series vol. 14, p. 153, and the account of certain analyses by Mr. Fownes, id. vol 15, p. 62.

as gas, this body is more suitable than any other substance to effect the reduction of metallic oxides, that is, to deprive them of their oxygen, and to produce from them the metal with the properties which characterize it.

CARBONIC ACID.

Eq. 276, or 22.13 ; CO_2 ; density 1524.1 ; .

This gas was first discovered to exist in lime-stone and the mild alkalies, and to be expelled from them by heat and the action of acids by Dr. Black, and was named by him Fixed Air. He also remarked that the same gas is formed in respiration, fermentation and combustion; it was afterwards proved to contain carbon by Lavoisier.

Preparation.—Carbonic acid is readily procured by pouring hydrochloric acid of sp. gr. 1.1, upon fragments of marble contained in a gas bottle, or by the action of diluted sulphuric acid upon chalk. A gas comes off with effervescence, which may be collected at the water trough, but cannot be retained long over water without considerable loss, owing to its solubility. When generated in the close apparatus of M. Thilorier for the purpose of liquefying it, this gas is evolved from bicarbonate of soda and sulphuric acid.

Properties.—This gas extinguishes flame, does not support animal life, and renders lime-water turbid. Its density is considerable, being 1524, or a half more than that of air, the gas containing 2 volumes of the hypothetical carbon vapour and 2 volumes of oxygen, condensed into 2 volumes, which form the combining measure. Cold water dissolves rather more than an equal volume of this gas; the solution has an agreeable acidulous taste, and sparkles when poured from one vessel into another. It communicates a wine-red tint to litmus paper, which disappears again when the paper dries; when poured into lime-water it first throws down a white flaky precipitate of carbonate of lime or chalk, which it afterwards redissolves if the solution be added in excess. The quantity of this gas which water takes up is found to be exactly proportional to the pressure; a very large volume of the gas is forced into soda, magnesia and other aerated waters, much of which escapes on removing the pressure from these liquids.

This gas was liquefied by Mr. Faraday, whose method has

been followed by Thilorier in an apparatus by which the liquid acid is procured in large quantity, which is constructed with some improvements by Mr. Addams of Kensington. It consists of two similar cylindrical vessels of strong sheet iron, calculated to resist a bursting pressure of 60 atmospheres, in one of which several pounds of bicarbonate of soda are decomposed at once by an equivalent quantity of sulphuric acid. The gas confined within this generating vessel is afterwards allowed to communicate with the second cylinder or condenser, by means of a copper tube and stopcock of nice construction; and the charge is repeated several times in succession, till two or three pints of the liquid acid are collected in the receiver. When this liquid is allowed to escape from the receiver by a small jet, a portion of it is frozen by its own evaporation, and forms a white soft mass, like snow, which may be handled and does not evaporate very rapidly, owing to its low conducting power, although its temperature cannot be more than -148° . With a little ether the solid acid forms a semifluid mass, by means of which mercury can be frozen in considerable quantity. The sp. gr. of the liquid is 0.83 at 32° ; it dilates remarkably from heat, its expansion being four times greater than that of air, 20 volumes of the liquid at 32° becoming 29 at 86° , and its density varying from 0.9 to 0.6 as its temperature rises from, -4° to 86° . It mixes in all proportions with ether, alcohol, naphtha, oil of turpentine and bisulphuret of carbon, but is insoluble in water and fat oils. Its compound with alcohol may be frozen, and melts at -135° , which is the lowest point fixed with accuracy in the descending scale of temperature.* Mr. Addams has made careful experiments upon the elasticity of the vapour of this liquid, at different temperatures, of which the following are the results:

ELASTIC FORCE OF LIQUID CARBONIC ACID.

Temperature.	Pounds per square inch.	Atmospheres of 15 pounds each.
0°	280	18.1
10	300	20
30	398	26.5
32	413	27.6
50	520	34.7
100	935	62.3
150	1496	99.7

* Thilorier, *An. de Ch. et de Ph.* t. 60, p. 427.

Potassium heated in a small glass bulb blown upon a tube, through which gaseous carbonic acid is transmitted, undergoes oxidation, and liberates carbon, the existence of which in the gas may thus be shown. But burning phosphorus, sulphur and other combustibles are immediately extinguished by carbonic acid, and the combustion does not cease from the absence of oxygen only, but from a positive influence in checking combustion which this gas exerts, for a lighted candle is extinguished in air containing no more than a fourth of its volume of carbonic acid. It is generally believed that any mixture of carbonic acid and air will support the respiration of man, which will maintain the flame of a candle, and therefore a lighted candle is often let down into wells or pits suspected to contain this gas, to ascertain whether they are safe or not. But although air in which a candle can burn may not occasion immediate insensibility, still the continued respiration for several hours of air containing not more than 1 or 2 per cent of carbonic acid, has been found to produce alarming effects (Broughton). The accidents from burning a pan of charcoal in close rooms are occasioned by this gas. It acts as a narcotic poison upon the system. A small animal thrown into convulsions from the respiration of this gas, may be recovered by sudden immersion in cold water.

Carbonic acid is thrown off from the lungs in respiration, as may be proved by directing a few expirations through lime water. The air of an ordinary expiration contains on an average, as observed by Dr. Prout, 3.45 per cent of the gas, and the proportion varies from 3.3 to 4.1 per cent, being greatest at noon, and least during the night. Carbonic acid is also a product of the vinous fermentation, and is the cause of the agreeable pungency of beer, ale and other fermented liquors, which become stale when exposed to the air from the loss of this gas. It also exists in all kinds of well and spring water, and contributes to their pleasant flavour, for water which has been deprived of its gases by boiling is insipid and disagreeable. Carbonic acid is also largely produced by the combustion of carbonaceous fuel, and appears to exist in considerable quantity in the earth, being discharged by active volcanoes, and from fissures in their neighbourhood long after the volcanoes are extinct. The Grotto del Cane in Italy owes its mysterious properties to this gas, and many mineral springs, such as those of Tunbridge, Pyrmont and Carlsbad are highly charged with it. It comes thus to be always

present in the atmosphere in a sensible although by no means considerable proportion. (page 280.)

Carbonic acid combines with bases, and forms the class of carbonates. The hydrate of this acid seems incapable of existing in an uncombined state, but it exists in the alkaline bicarbonates, which are double carbonates of water and the alkali. If this hydrate were formed, it would probably be found analogous to the crystallized carbonate of magnesia, of which the formula is $\text{MgO}, \text{CO}_2 + \text{HO} + 2\text{HO}$, and also the same with another 2HO ; the salt of magnesia of most acids resembling the salt of water. Carbonate of lime, in the hydrated condition, has a similar formula. But the carbonates exhibit little affinity for water, and are generally anhydrous. Those of the alkalis retain a strong alkaline reaction, owing to the weakness of this acid, and the carbonates generally are decomposed with effervescence by all other acids, except hydrocyanic.

Uses.—Carbonic acid is not used in the arts, except in the preparation of aerated waters. The strong vessels in which the impregnation is effected, should be of copper well tinned, and not of iron, as with the concurrence of water carbonic acid acts strongly upon that metal. It is sometimes desirable to remove carbonic acid from air or other gaseous mixtures, and this is generally done by means of caustic alkali or lime-water. When very dry, or so humid as to be actually wet, the hydrate of lime absorbs this gas with much less avidity than when of a certain degree of dryness, in which it is not so dry as to be dusty, but at the same time not sensibly damp. The dry hydrate may be brought at once to this condition, by mixing it intimately with an equal weight of glauber's salt, in fine powder; and this mixture in a stratum of not more than an inch in thickness intercepts carbonic acid most completely, and may rise in temperature to above 200° from the rapid absorption of the gas. It is quite possible to respire through a cushion of that thickness, filled with this mixture, and such an article might be found useful by parties entering an atmosphere overcharged with carbonic acid, like that of a coal mine after the occurrence of an explosion of fire damp.

Carbonic acid is the highest degree of oxidation of which carbon is susceptible; but another oxide of carbon exists containing less oxygen.

CARBONIC OXIDE.

Eq. 176, or 14.13; CO; *density* 972.8; .

Priestley is the discoverer of this gas, but its true nature was first pointed out by Cruikshanks, and about the same time by Clement and Desormes.

Preparation.—Carbonic acid is readily deprived of half its oxygen, at a red heat, by a variety of substances, and so reduced to the state of carbonic oxide. The latter gas may therefore be obtained by transmitting carbonic acid over red hot fragments of charcoal contained in an iron or porcelain tube; or by calcining chalk mixed with 1-4th of its weight of charcoal in an iron retort. It is likewise prepared by gently heating crystallized oxalic acid with 5 or 6 times its weight of strong oil of vitriol in a glass retort. The latter process affords a mixture of equal volumes of carbonic acid and carbonic oxide, the elements of oxalic acid being carbon and oxygen in the proportion to form these gases, and this acid being incapable of existing except in combination with water or some other base. Now the sulphuric acid unites with the water of the cr. oxalic acid, and the acid being set free is instantly decomposed. The gas of all these processes contains much carbonic acid, of which it may be deprived, by washing it with milk of lime, or by transmitting the gas through a tube filled with the mixture of hydrate of lime and glauber's salt.

Properties.—This gas, as has already been stated, is presumed to contain 2 volumes of carbon, and 1 volume of oxygen, condensed into 2 volumes so that its combining measure is 2 volumes. It is not more soluble in water than atmospheric air, and has never been liquefied. It is easily kindled and burns with a pale blue flame, like that of sulphur, combining with half its volume of oxygen, and forming carbonic acid, which retains the original volume of the carbonic oxide. This combustion is often witnessed in a coke or charcoal fire. The carbonic acid produced in the lower part of the fire, is converted into carbonic oxide, as it passes up through the red hot embers, and afterwards burns above them with a blue flame, where it meets with air.

Carbonic oxide is a neutral body, like water, and combines directly with only a very few substances. It unites with an equal

volume of chlorine under the influence of the sun's rays, and forms *phosgene* gas or chlorocarbonic acid. It is also absorbed by potassium gently heated, and that metal is employed to separate carbonic oxide from a mixture of hydrogen and gaseous hydrocarburets, as in the analysis of coal gas. But carbonic oxide is supposed to exist in a greater number of compounds, and to be the radical of a series, of which the following substances are imagined to be members :

CARBONIC OXIDE SERIES.

Carbonic oxide.	CO
Carbonic acid.	CO + O
Chlorocarbonic acid.	CO + Cl
Oxalic acid.	2CO + O
Oxamide.	2CO + NH ₂
Oxcarburet of potassium.	7CO + 3K
Croconic acid.	5CO + H
Mellitic acid.	4CO + H

In these compounds carbonic oxide is represented as playing the part of a simple substance, and forming a variety of products by uniting with oxygen, chlorine, hydrogen and other elements.

Oxalic, mellitic and croconic acids are sometimes enumerated as oxides of carbon, along with carbonic acid and carbonic oxide, but as the former bodies always exist in a state of combination and cannot be isolated, they have not an equal claim to the same early consideration as the latter compounds.

SECTION V.

BORON.

Eq. 136.25, or 10.91; B; density of vapour (hypothetical) 751; .

Boron is an element having some analogy to carbon, but sparingly diffused in nature. It is never found, except in combination with oxygen as boracic acid, of which the salt of soda has long been brought to Europe from India in a crude state, under the name of tinkal and termed borax when purified. The impure borax or tinkal forms a saline incrustation in the beds of certain small lakes in an upper province of Thibet, which dry up

during summer. But the most considerable of the present sources of boracic acid are the hot lagoons of a district in Tuscany, which are charged with the free acid, from the condensation in them of vapours of a volcanic origin. Boracic acid is likewise found in the hot springs of Lipari. It is a constituent also of several minerals, of which datolite and boracite are the most remarkable. Boron was first discovered by Sir H. Davy in 1807, by exposing boracic acid to the action of a powerful voltaic battery, and was afterwards obtained by Gay-Lussac and Thenard in greater quantity, by heating boracic acid with potassium.

Preparation.—Boron is prepared with greatest advantage from a combination of fluoride of boron and fluoride of potassium, which is obtained on saturating hydrofluoric acid with boracic acid, and adding to it drop by drop, the fluoride of potassium. This compound which is of slight solubility, is collected on a filter, and dried at an elevated temperature, but which should not reach a red heat. Equal weights of this compound and potassium are mixed together in a cylinder or tube of iron, closed at one end, which is gently heated, and the mixture stirred with an iron rod, till the potassium is melted. Heated more strongly by a spirit lamp, the mass evolves heat and becomes red-hot; the potassium combines with the fluorine, and a mixture is obtained of boron and the fluoride of potassium. On treating this with water, the fluoride of potassium dissolves, and the boron remains insulated. In washing it farther, instead of pure water, which acts upon boron, a solution of sal ammoniac should be employed, which does not dissolve that body, and the sal ammoniac remaining in the boron may be taken up by alcohol.

Properties.—Thus prepared, boron is obtained in the form of a greenish brown powder, without the metallic lustre, which becomes hard and assumes a deeper colour, when ignited in vacuo, or in gases which do not combine with it, but undergoes no farther change. Heated in atmospheric air or oxygen it burns with a vivid light, scintillating powerfully, and forms boracic acid. Nitric acid and many other substances also oxidate it easily, and always produce that compound. Fused with carbonate of potash, it decomposes the carbonic acid, and gives borate of potash, carbon being liberated. Boron is not known to possess any other degree of oxidation. Boron com-

bines with sulphur, with the disengagement of light, when heated in the vapour of that substance ; and it takes fire spontaneously in chlorine, and forms a gaseous chloride of boron, of which the formula is BCl_3 , and the density 4.035. This gas is formed of 2 vols. of boron vapour and 6 of chlorine, condensed into 3 vols. which are its combining measure. It may likewise be formed, by transmitting chlorine gas over a mixture of boracic acid and charcoal, ignited in a porcelain tube. A corresponding fluoride of boron is evolved from boracic acid, ignited with the fluoride of calcium or fluor spar, with the formation of borate of lime. The density of this fluoride is 2.308.

Boracic acid.—This acid is generally prepared by dissolving the salt borax at 212° in four times its weight of water, the solution is filtered hot, and a quantity of oil of vitriol immediately added to it, equal to one fourth of the weight of the borax. The sulphuric acid unites with the soda, and forms sulphate of soda, which continues in solution, while the boracic acid separates in thin shining crystalline plates, on cooling. These plates are drained, and being sparingly soluble, may be washed with cold water, and afterwards redissolved in boiling water and made to crystallize anew. The boracic acid still retains a small quantity of sulphuric acid, probably in a state of chemical combination, and if required of absolute purity must be fused at a red heat in a platinum crucible, then dissolved again and crystallized. The density of the vitrified acid is 1.83. Boracic acid has a weak taste, which is scarcely acid, and affects blue litmus like carbonic acid, imparting to it a wine-red tint, and not that clear red, free from purple, which the stronger acids produce. It renders yellow turmeric paper, brown, like the alkalies. The crystals are a hydrate, and contain 3 equivalents of water, of which the formula is $\text{HO}, \text{BO}_3 + 2\text{HO}$. At 60° it requires 25.66 times its weight of water to dissolve it, but only 2.97 times at 212° . With the assistance of the vapour of water, it is said to be slightly volatile, but alone it is fixed, and fuses, under a red heat, into a transparent glass. The hydrated acid dissolves in alcohol, and the solution burns with a fine green flame. At the temperature of the air, boracic acid is relatively a feeble acid, but at a red heat it displaces the greater number of those acids which are more volatile than itself. It communicates fusibility to many substances in uniting with them, and generally forms a glass. On this account borax is much used as a flux.

Borates.—Boracic acid is remarkable for the variety of proportions in which it unites with the alkalis; all these borates have an alkaline reaction like the carbonates. The relative proportions of oxygen and boron in boracic acid are known, but the number of equivalents of these elements in this acid is not so certain. Dumas inferred from the density of the chloride that it is a terchloride, and boracic acid, which corresponds, will therefore consist of 3 eq. oxygen to 1 eq. boron, and its formula be BO_3 . This makes borax the biborate of soda.

SECTION VI.

SILICON.

Syn. SILICIUM. *Eq.* 277.31 or 22.22; Si O_3 ; *density of vapour (hypothetical)* 1529; .

Silica or siliceous earth, the oxide of the present element, is the most abundant of all the matters which compose the crust of the globe. It constitutes sand, the varieties of sandstone and quartz rock, and enters into felspar, mica and a prodigious variety of minerals, which form the basis of other rocks.

Preparation.—Silica may be decomposed by heating it with potassium, which deprives it of oxygen; but a better process for obtaining silicon, is to heat the double fluoride of silicon and potassium, with 8 or 9-10ths of its weight of potassium, with the same precautions as in the preparation of boron. The materials, however, in this case may be heated in a glass tube, as well as in an iron cylinder. The double fluoride employed, is prepared by neutralizing fluosilicic acid with potash. A different process is suggested by Berzelius, which consists in heating potassium in a tube of hard glass with a small bulb blown upon it, which is filled with the vapour of the fluoride of silicon, supplied from the ebullition of that liquid contained in a small retort connected with the glass tube. The potassium burns in this vapour, and at the end, silicon is found, with fluoride of potassium, in the place of the metal (*Traité*, t. 1, p. 137). But the silicon from all these processes is always in combination with a little potassium, and mixed with a little fluoride of

silicon and potassium unreduced. Hence, on applying cold water to the mass, hydrogen gas is disengaged, and potash formed, and the silicon separates. The potash thus produced can, with the aid of hot water, dissolve the silicon, which then oxidates and becomes silica, so that cold water only must be employed to wash the silicon, which may be thrown upon a filter. After a time, the liquid which passes has an acid reaction, which arises from its dissolving an acid double fluoride of silicon and potassium, of sparing solubility, which has escaped decomposition, and is mixed with the silicon. The washing is continued so long as the water dissolves anything.

Properties.—The silicon which is thus obtained is, in its pure state, a dull brown powder, which soils the fingers, and when heated in air or oxygen, inflames and burns, but is never more than partially converted into silica. It may be ignited strongly in a covered crucible without loss, and then shrinks in dimensions, acquires a deep chocolate colour, and becomes so dense as to sink in oil of vitriol. By this ignition the properties of silicon are altered to a degree which is very remarkable in a simple substance. It was previously readily soluble in hydrofluoric acid, with evolution of hydrogen, and in caustic potash, but it is now no longer acted upon by that or any other acid, nor by alkalies. The ignited silicon also refuses to burn in air or oxygen, even when intensely heated by the blow-pipe flame. Charcoal, it will be remembered, is more dense and less combustible after being strongly heated; but that substance is not altered by heat to the same extent as silicon. Mixed and heated with dry carbonate of potash, silicon in any condition is oxidated completely, its action upon the carbonic acid of the salt being attended with ignition, and carbon liberated. Silicon burns when heated in sulphur vapour, and forms a sulphuret, which water dissolves, but decomposes at the same time, sulphuretted hydrogen and silica being produced, and the last, despite its usual insolubility, retained in solution. Silicon likewise burns in chlorine; and the chloride of silicon may be otherwise formed by transmitting chlorine over a mixture of charcoal and silica ignited in a porcelain tube. The silica is decomposed by neither charcoal nor chlorine singly, but acting together upon the silica, these bodies produce carbonic oxide and chloride of silicon. This compound is a vola-

tile liquid, of which the formula is Si Cl_3 ; that of the sulphuret of silicon Si S_3 .

Silica or Silicic Acid, Si O_3 .—This earth, which is the only oxide of silicon, constitutes a number of minerals, nearly in a state of purity, such as rock-crystal, quartz, flint, sandstone, the amethyst, calcedony, cornelian, agate, opal, &c. The first chemical examination of its properties and compounds is due to Bergman.

Preparation.—Silica may be had very nearly, if not absolutely pure, by heating a colourless specimen of rock crystal to redness and throwing it into water, after which treatment the mineral may easily be pulverized. It is obtained in a state of more minute division, by transmitting the gaseous fluoride of silicon (fluosilicic acid) into water; or by the action of acids upon some of the alkaline compounds of silica. Equal parts of carbonate of potash and carbonate of soda may be fused in a platinum crucible, at a temperature which is not high; and pounded flint or any other siliceous mineral, thrown by little and little into the fused mass, dissolves in it with an effervescence due to the escape of carbonic acid gas. The addition of the mineral may be continued so long as it determines this effervescence. The mass being allowed to cool, is afterwards dissolved in water acidulated with hydrochloric acid, which takes up the silica as well as the alkalies; the liquor is filtered and then evaporated to dryness. The silica may contain a little peroxide of iron or alumina, to dissolve which the saline mass, when perfectly dry, is moistened with concentrated hydrochloric acid, and after two hours the acid mass is washed with hot water. The silica remains undissolved; it may be dried well and ignited.

Properties.—Silica so prepared is a white, tasteless powder, which is rough to the touch, and feels gritty between the teeth. It is extremely mobile when heated, and is thrown out of a crucible, at a high temperature, by the slightest breath of wind. It is absolutely insoluble in water, acids and most liquids. Its density is 2.66. The heat of the strongest wind-furnace is not sufficient to fuse silica, but it melts into a limpid colourless glass in the flame of the oxihydrogen blow-pipe. Silica is found frequently crystallized, its ordinary form being a six-sided prism terminated by a six-sided pyramid, as in rock-crystal. Some-

times the prism is very short or disappears entirely, and the pyramid only is seen, as in ordinary quartz.

Soluble Silicic Acid.—The preceding description applies to silica after it has been dried or heated, but silica can also be obtained in a state in which it is soluble in dilute acids and even in water. The oxidation of the sulphuret of silicon, in water, gives silica in this condition; the solution when concentrated, becomes a gelatinous mass, like size. When the gaseous fluoride of silicon is absorbed by water, silica separates in large quantity in that gelatinous condition, and this jelly is soluble in water although it requires a large quantity to dissolve it. The solution of silica was found by Berzelius to be insipid, and not to redden litmus; by evaporation of the liquor the silica is deposited in the form of an earthy mass without a trace of crystallization, and capable of dissolving again in water. It is observed however, that when sulphuric or hydrochloric acid is added to the solution during evaporation, the silica obtained is no longer the soluble, but the former insoluble variety. The fixed alkalis and their carbonates, it is curious, effect a transmutation of the opposite kind, for when insoluble silica is boiled with them, it is gradually converted into the soluble species and dissolves. Berzelius finds that this change supervenes, without decomposition of the alkaline carbonate or any escape of carbonic acid. The alkali in this solution may be saturated completely with an acid, without any silica precipitating, which proves that that body is dissolved in the water and not in the alkaline carbonate.

The water of springs and wells always contains a little soluble silica, which can only be obtained by evaporating the water to dryness. In some mineral waters the proportion of silica is very considerable, and it is often associated with an alkaline carbonate, as in the hot alkaline spring of Reikum in Iceland, and in the boiling jets of the Geyser, which deposit about their crater an incrustation of silica. There can be no doubt likewise that much of the crystalline quartz in nature besides all the agates, calcedonies and siliceous petrifications have been formed from an aqueous solution.

The soluble silica seems to exist in the class of minerals called *zeolites*, which also contain water, and many of which dissolve entirely in dilute hydrochloric acid. But it may be obtained from any silicate by fusing it with an alkaline carbo-

nate, and afterwards dissolving in dilute acid. The solution, on concentration, gives a transparent jelly, which is highly tenacious, and cracks on drying, forming a mass like gum. When completely dried in the air, the mass is no longer soluble in water or acids. It contains a small quantity of water, which however, according to Berzelius is hygroscopic; silica affording him no definite hydrates, like those of other acids. But I should still be disposed to look to the state of hydration, however feebly the water may be retained, for an explanation of the differences between the soluble and insoluble varieties of silica. Hydrofluoric acid is the only acid which dissolves silica in both conditions.

Silicates.—Although silica has no acid reaction, it is certainly an acid, and is indeed capable of displacing the most powerful of the volatile acids at a high temperature. It is capable of uniting with metallic oxides, by way of fusion, in a great variety of proportions. Its compounds with excess of alkali, are caustic and soluble, but those with an excess of silica are insoluble, and form the varieties of *glass*, which will be noticed under the silicate of soda. With alumina it forms the less fusible compounds of porcelain and stoneware which will be noticed under that earth. A large number of mineral species are also earthy silicates. It seems probable that silicic, like phosphoric acid, forms several classes of salts, of which those containing the largest number of atoms of base are the most soluble, and afford, when decomposed the soluble silica. At the same time some difference may exist between the silicic acid itself, as it exists in these different classes of salts, such as there is between ignited and unignited silicon.

SECTION VII.

SULPHUR.

Eq. 201.17 or 16.12; S; *density* 6648; *combining measure* 1-3rd. volume.

This element is exhaled in large quantity from volcanoes, either in a pure state or in combination with hydrogen, and by condensing in fissures forms sulphur veins, from which the greater part of the sulphur of commerce is derived. It exists

also in combination with many metals, as iron, lead, copper, zinc, &c.; and is extracted in considerable quantity from bisulphuret of iron or iron pyrites. Sulphur is classed with oxygen; and the higher sulphurets resemble peroxides in losing a portion of their sulphur, as we have seen some of the latter lose a portion of their oxygen, when strongly heated. Sulphur is likewise extensively diffused, as a constituent of the sulphuric acid in gypsum and other native sulphates. This element also enters the organic kingdom, being invariably associated in minute quantity with albumen, whether fluid in the egg or solid in the hair.

Properties.—Sulphur is found in commerce in rolls, which are formed by pouring melted sulphur into cylindrical moulds, and also in the form of a fine crystalline powder, the flowers of sulphur, which are obtained by throwing the vapour of sulphur into a close apartment, of which the temperature is below the point of fusion of that substance, and in which the sulphur therefore condenses in the solid form and in minute crystals, just as watery vapour does in the atmosphere below 32° , in the form of snow. The purity of the flowers is more to be depended upon than that of roll sulphur. Sulphur is insipid, and generally inodorous, but acquires an odour when rubbed; it is very friable, a roll of it generally emitting a crackling sound, and sometimes breaking, when held in the warm hand. Its specific gravity is 1.98. It fuses at 226° , and between that temperature and 280° forms a clear liquid of an amber colour. But about 320° it begins to thicken, assumes a reddish tint, and if the heat be continued, becomes so thick that the vessel may be inverted without the sulphur flowing out. This change is not occasioned by an increase of density, for fluid sulphur continues to expand with the temperature. Thrown into water, while in this condition, sulphur forms a mass which remains soft and transparent for some time after it is perfectly cool, and may be drawn into threads which have considerable elasticity. From 482° to its boiling point 601° , it becomes again more fluid, and if allowed to cool returns through the same conditions, becoming again very fluid, before freezing. Sulphur has considerable volatility, beginning to rise in vapour before it is completely fused. At its boiling point it forms a vapour of an orange colour, and distils over unchanged. The density of this vapour is very considerable, being observed to lie between

6510 and 6617 by Dumas, and to be 6900 by Mitscherlich. It is allowed that the combining measure of this vapour is 1-3rd of a volume, which gives the theoretical density 6648.

Sulphur and many other substances may be obtained in distinct crystals, on passing from a state of fusion, by operating in a particular manner. A considerable quantity of sulphur is fused in a stoneware crucible, and allowed to cool till it begins to solidify; the solid crust, with which its surface is covered, is then broken, and the portion remaining fluid poured out. On afterwards breaking the crucible, when it has become quite cold, the sulphur is found to have a considerable cavity which is lined with fine crystals, like a geode in quartz. Sulphur is dimorphous, the form which it assumes at a high temperature, and consequently in its passage from a state of fusion, is a secondary modification of an oblique prism with a rhomboidal base. Sulphur is also soluble in the sulphuret of carbon, the chloride of sulphur and oil of turpentine, and is deposited from solution in these menstrua at a lower temperature, and of its second form, which is an elongated octohedron with a rhomboidal base. That is likewise the form of the grains of flowers of sulphur, and of the fine transparent crystals of native sulphur, which are also formed by sublimation.

Sulphur is not soluble in water or in alcohol. It combines readily with most metals, some of them, such as copper and silver in very thin plates, burning in its vapour, as iron does in oxygen gas. When iron and some other metals are mixed in a state of division with flowers of sulphur and heat applied, the sulphur first melts, and after a few seconds combination ensues with turgescence of the mass, which becomes red hot. Sulphur unites with bodies generally in the same multiple proportions as oxygen, and sometimes in additional proportions, particularly with potassium and the metals of the alkalies and alkaline earths. When boiled with caustic potash or lime, red solutions are formed which contain a large quantity of sulphur, a considerable proportion of which is deposited as a white hydrate of sulphur, upon the addition of an acid. With hydrogen, sulphur unites in single equivalents, and forms sulphuretted hydrogen gas, which is the analogue of water in the sulphur series of compounds, and also another compound the persulphuret of hydrogen, which is deficient in stability, like the

peroxide of hydrogen, and is decomposed or preserved by similar agencies.

Sulphur is readily inflamed, taking fire below its boiling point and burning with a pale blue flame, and the formation of suffocating fumes, which are sulphurous acid gas. It exhausts the oxygen of a confined portion of air by its combustion, more completely than carbonaceous combustibles, and on that account, and partly also from a negative influence which sulphurous acid has upon the combustion of other bodies, it may be employed in particular circumstances to extinguish combustion; a handful of lump sulphur being dropt into a burning chimney as the most effectual means of extinguishing it. Sulphur unites directly with oxygen only in the proportions of sulphurous acid, but several compounds of the same elements may be formed, which are all acids; namely

Hyposulphurous acid.	$S_2 O_2$
Sulphurous acid.	$S O_2$
Hyposulphuric acid.	$S_2 O_5$
Sulphuric acid.	$S O_3$

Uses.—From its ready inflammability sulphur has long been applied to wood-matches. But its most considerable applications are in the composition of gunpowder and other deflagrating mixtures, and in the manufacture of sulphuric acid, which there will again be occasion to notice in a more particular manner.

SULPHUROUS ACID.

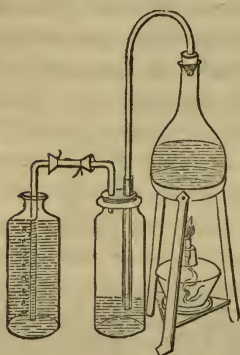
Eq. 401.17, or 32.12; SO_2 ; density 2210.6; combining
measure .

Sulphurous acid was distinguished as a particular substance by Stahl, and first recognized as a gas by Dr. Priestley. It was subsequently analyzed with accuracy by Gay-Lussac and by Berzelius.

Preparation.—When sulphur is burned in dry air or oxygen gas, sulphurous acid is the sole product, and the gas is found to have undergone no change in volume. But sulphurous acid is more conveniently prepared by heating oil of vitriol upon mercury or copper, either of which becomes an oxide at the expense

of one portion of the sulphuric acid, and thereby causes the formation of sulphurous acid. Charcoal, chips of wood, straw and such bodies occasion a similar decomposition of sulphuric acid, when heated with it, but the gas is then mixed with a large quantity of carbonic acid. If the sulphurous acid, however, is to be used to impregnate water, or in making alkaline sulphites, the presence of that gas is immaterial. With that object, a quantity of oil of vitriol, equal in volume to 4 ounce measures of water, which for brevity may be spoken of as 4 ounce measures of oil of vitriol, may be introduced into a flask (see figure) with

FIG. 36.



$\frac{1}{2}$ ounce of pounded charcoal, and the two substances well mixed with agitation. Effervescence takes place, upon applying heat to the flask, from the evolution of gas, which may be conducted in the first instance into an intermediate phial, through the cork of which a stout tube passes, open at both ends and about 3-8ths of an inch in internal diameter. This phial contains about an ounce of water, into which the tube dips, and serves the purpose of condensing any sul-

phuric acid vapour, that may be carried over by the gas, or of intercepting the liquid material in the flask, if thrown out by ebullition, and also of preventing the liquid in the second bottle from passing back, by the gas tube, into the generating flask, on the occurrence of a contraction of the air in that flask, by cooling or any other cause. When that contraction happens in this arrangement, the external air enters the intermediate phial by its open tube. The second bottle is nearly filled with the liquid to be impregnated by the gas. This is the form in most frequent use of the Wolfe's bottles, employed in transmitting a stream of gas through a liquid.

Water at 60° is capable of dissolving 37 times its volume of sulphurous acid, which makes it necessary to collect this gas for examination in jars filled with mercury in the mercurial trough, and not over water. Its density is 2210.6, and it contains 2 volumes of oxygen with 1-3rd of a volume of sulphur vapour, condensed into 2 volumes, which form its combining measure. It may easily be obtained in the liquid state by transmitting the dry

gas through a tube surrounded by a freezing mixture of ice and salt, and forms a colourless and very mobile liquid, of sp. gr. 1.45, which boils at 14°. The volatility of this liquid is small at considerably lower temperatures, and it is not applicable with advantage to produce intense cold by its evaporation (Mr. Kemp). With a little water, it forms a crystalline hydrate, which contains 20 per cent of acid, and perhaps therefore 14 equivalents of water.

Sulphurous acid is not decomposed by a high temperature; but several substances such as carbon, hydrogen and potassium, which have a strong affinity for oxygen, decompose it at a red heat. This acid blanches many vegetable and animal colours, and the vapours of burning sulphur are therefore employed to whiten straw, and to bleach silk, to which they also impart a peculiar gloss. The colours are not destroyed, and may in general be restored by the application of a stronger acid or an alkali. Dry sulphurous acid exhibits no affinity for oxygen, but in contact with a little water, these gases slowly combine and sulphuric acid is formed. From the same affinity for oxygen, sulphurous acid deprives the solution of chameleon mineral of its red colour, and throws down iodine from iodic acid. It decomposes the solutions of those metals which have a weak affinity for oxygen, such as gold, silver and mercury (with heat), and throws down these bodies in the metallic state. Sulphurous acid is conveniently withdrawn from a gaseous mixture by means of peroxide of lead, which is converted by absorbing this gas into the white sulphate of lead. By nitric acid, sulphurous acid is immediately converted into sulphuric acid.

Sulphites.—The alkaline sulphites have a considerable resemblance to the corresponding sulphates. Their acid is precipitated by the chloride of barium, but the sulphite of barytes is dissolved by hydrochloric acid. Sulphurous acid is a weak acid and its salts are decomposed by most other acids.

Uses.—Besides the application of which sulphurous acid is susceptible in bleaching, it is likewise employed in French hospitals, in the treatment of diseases of the skin. The gas is then applied in the form of a bath. (Dumas, *Traité de Chimie appliquée aux Arts*, t. 1, p. 151).

This oxide of sulphur, besides acting as an acid, appears to play the part of a radical, like carbonic oxide, and to pervade a

class of compounds, in which hyposulphurous acid and sulphuric acid are included.

SULPHUROUS ACID SERIES.

Sulphurous acid.	SO_2
Sulphuric acid.	$\text{SO}_2 + \text{O}$
Hyposulphurous acid.	$\text{SO}_2 + \text{S}$
Chlorosulphuric acid.	$\text{SO}_2 + \text{Cl}$
Iodosulphuric acid.	$\text{SO}_2 + \text{I}$
Nitrosulphuric acid.	$\text{SO}_2 + \text{NO}_2$

SULPHURIC ACID.

Eq. 501.17, or 40.12; SO_3 ; *density* 2762; .

Chemists have been in possession of processes for preparing this acid since the end of the fifteenth century. It is of all reagents the one in most frequent use, being the key to the preparation of most of the other acids, which, in consequence of its superior affinities, it separates from their combinations, and being the acid preferred to others from its cheapness, for various useful and important purposes in the arts.

Preparation.—Sulphuric acid was first obtained by the distillation of green vitriol or copperas, a native sulphate of iron, and this process is still followed at Nordhausen in Saxony, for the preparation of a highly concentrated acid. The sulphate of iron contains seven equivalents of water, and is first dried, by which its water is reduced considerably below a single equivalent, and then distilled in a retort of stoneware at a red heat. When the experiment is performed on a small scale, the heat of an argand spirit lamp is sufficient; and in the place of copperas, the sulphate of iron previously peroxidized, the sulphate of bismuth, of antimony, or of mercury may be employed. The first effect of heat upon the dried copperas, is to cause an evolution of sulphurous acid gas, a portion of sulphuric acid being decomposed in converting the protoxide of iron of that salt into peroxide. Vapours afterwards come over, which condense into a fuming liquid, generally of a black colour, and of a density about 1.9, which is the Nordhausen acid, and contains less than one equivalent of water to two of sulphuric acid. This acid is preferred for dissolving indigo, and for some other purposes in the arts, and is the best source of anhydrous sulphuric acid.

But sulphuric acid is prepared, in vastly greater quantity, by the oxidation of sulphur. When burned in air or oxygen, sulphur does not attain a higher degree of oxidation than sulphurous acid, but an additional proportion of oxygen may be communicated to it by two methods, and sulphuric acid formed.

1°. When a mixture of sulphurous acid and air is made to pass over spongy platinum at a high temperature, the sulphurous acid is converted into sulphuric acid at the expense of the oxygen of the air. Mr. Peregrine Phillips, who first made this observation, has founded upon it a method of preparing sulphuric acid on the large scale, which, although not yet sufficiently tried to establish its advantage as a manufacturing process, is still of great interest in a scientific point of view, and deserves consideration. Sulphur is burned, or iron pyrites in place of it, and the sulphurous acid produced, is mixed with an excess of air, by a blowing apparatus, and carried through a tube filled with the platinum sponge or balls of fine platinum wire. The vapours of sulphuric acid formed, which are mixed with the nitrogen of the air, are condensed in a long and narrow vessel of lead, in an upright position, filled with pebbles, which are kept constantly wet by a small stream of water, admitted at the top and which percolates downwards.

2°. Sulphurous acid mixed with air may likewise be converted into sulphuric acid, by the agency of nitric oxide, which is the process generally pursued in the manufacture of that acid. The theory of this latter method, which is by no means obvious, was established by the researches of Clement Desormes and of Sir H. Davy. When nitric oxide mixes with air in excess, it instantly combines with oxygen, and becomes in a great measure peroxide of nitrogen, or NO_4 . If dry sulphurous acid gas, SO_2 , be mixed with that compound, no change occurs, the two gases when dry having no action upon each other. But if a little moisture, in the state of vapour be admitted to the mixture, then oxygen is transferred from the peroxide of nitrogen to the sulphurous acid, the former becoming nitrous acid NO_3 , and the latter sulphuric acid SO_3 ; and these two acids, in combination with each other and with a portion of water, precipitate as a crystalline solid, a kind of sulphate of nitrous acid, of which the exact composition has been already given (page 289). The effect of an additional small quantity of

water upon this crystalline solid is remarkable, occasioning its decomposition with effervescence; a hydrate of sulphuric acid remains behind, and the nitrous acid is expelled in a state of decomposition, as nitric oxide and peroxide of nitrogen. The result then of these changes has been the formation of a certain quantity of sulphuric acid; and the nitric oxide is again restored to the gaseous atmosphere; where if it meets a second time with oxygen, sulphurous acid and moisture, it may give occasion to a repetition of the same changes, and the formation of an additional proportion of sulphuric acid, and do so again and again, so long as it continues to meet with both oxygen, sulphurous acid, and moisture. The nitric oxide is thus a medium of transference, by which the oxygen of the air reaches the sulphurous acid, and a small portion of the former may be the means of converting a large quantity of the latter into sulphuric acid.

In the manufacture upon the large scale, the sulphurous acid is converted into sulphuric acid, in oblong chambers of sheet-lead, supported by an external framework of wood. Sulphurous acid from burning sulphur, nitric acid vapour and steam are simultaneously admitted into the leaden chamber; and the sulphuric acid formed accumulates in the liquid state upon the floor of the chamber. The diagram below represents one of the most improved forms of the chamber, with its appendages.

FIG. 37.



a represents the water boiler, with its furnace for supplying the chamber with steam; *b*, the section of a small chamber in brickwork, or furnace, called the burner, upon the floor of which the sulphur burns, and in which there is a tripod supporting an iron capsule, which contains the materials for nitric acid, namely oil of vitriol and either nitre or nitrate of soda. The heat of the burning sulphur evolves the nitric acid from these materials, and consequently the sulphurous acid becomes mixed with nitric acid vapour, which it carries forward with it, by a tube represented in the figure, into the chamber, where

these acid vapours meet with the steam admitted near the same point, and the formation of sulphuric acid takes place. The nitric acid vapour is equivalent to nitric oxide or peroxide of nitrogen, as the first effect of the sulphurous acid is to reduce the nitric acid to a lower state of oxidation. From 8 to 19 parts of sulphur are consumed in the burner for 1 part of nitre decomposed there, so that the quantity of nitrous fumes is small compared with the quantity of sulphurous acid thrown into the chamber. The chamber itself is 72 feet in length by 14 in breadth and 10 in height, and is divided into three compartments, by leaden curtains placed across it, two of which, *d* and *f*, are suspended from the roof, and reach to within six inches of the floor, and one *e* rises from the floor to within six inches of the roof. *g* is a leaden conduit tube, for the discharge of the uncondensable gases, which should communicate with a tall chimney, to carry off these gases and to occasion a slight draught through the chamber. The curtains serve to detain the vapours, and cause them to advance in a gradual manner through the chamber, so that the sulphuric acid is deposited as completely as possible, before the vapours reach the discharge tube. When the oxygen of the chamber is exhausted, the admission of acid vapours is discontinued, till the air in it is renewed. But the admission of air to the chamber is sometimes so regulated, that a continuous current is maintained through the chamber, and the combustion proceeds without interruption. When steam is admitted in proper quantity, as in this method, it is not necessary to begin by covering the floor with water, as the sulphuric acid is condensed without it.

The acid may be drawn off from the floor of the chamber of a sp. gr. as high as 1.6. It is further concentrated in open leaden pans, till it begins to act upon the metal and afterwards in retorts of platinum or glass. It still retains small quantities of nitrous acid and sulphate of lead, from which it can be completely purified by dilution with water and a second distillation. The acid thus obtained in its most concentrated state is a definite compound of one atom acid and one atom of water, which last cannot be separated by heat, the hydrate distilling over unchanged. It is the oil of vitriol of commerce.

Properties.—Anhydrous sulphuric acid is obtained by gently heating the fuming acid of Nordhausen in a retort, and

receiving its vapour in a bottle artificially cooled, which can afterwards be closed by a glass stopper. It condenses in solid fibres, like asbestos, which are tenacious and may be moulded by the fingers like wax. Its density at 68° is 1.97. At 77° it is liquid, and a little above that temperature it enters into ebullition, affording a colourless vapour, which produces dense white fumes on mixing with air, by condensing the moisture in it. The dry acid does not redden litmus, an effect, which requires the presence of moisture. It combines with sulphur, and produces compounds which are of a brown, green and blue colour, and with one tenth of its weight of iodine forms a compound of a fine green colour, which assumes the crystalline form. Heated in the acid vapour, caustic lime or barytes inflames and burns for a few seconds; the vapour is absorbed, and sulphate of lime or barytes formed. The anhydrous acid has a great affinity for water, and when dropped into that liquid, occasions a burst of vapour, from the heat evolved. The density of its vapour was found to be 3000 by Mitscherlich, but it is probably 2762, and formed of 3 volumes of oxygen and 1-3rd of a volume of sulphur vapour, condensed into 2 volumes, which constitute its combining measure. This vapour is resolved by a strong red heat into sulphurous acid and oxygen.

When the Nordhausen acid is retained below 32° , well formed crystals appear in it, which Mitscherlich finds to be a compound of two equivalents of acid, and one of water, or $2\text{SO}_3 + \text{HO}$.* This compound is resolved by heat into the anhydrous acid, which sublimes, and the first hydrate, or oil of vitriol.

The most concentrated oil of vitriol of the leaden chambers ($\text{HO} + \text{SO}_3$) is a dense, colourless fluid, of an oily consistence which boils at 620° , and freezes at -29° , yielding often regular six sided prisms of a tabular form. It has a specific gravity at 60° of 1.847 or a little higher, but never exceeding 1.850. It is a most powerful acid, supplanting all others from their combinations, with a few exceptions, and when undiluted is highly corrosive. It chars and destroys most organic substances. It has a strong sour taste, and reddens litmus even though greatly diluted. Sulphur is soluble to a small extent in the concentrated acid, and communicates a blue, green or brown

* *Elémens de Chimie*, par E. Mitscherlich, t. 2, p. 57.

tint to it; so are selenium and tellurium. Charcoal also appears to be slightly soluble in this acid, imparting to it a pink tint, which afterwards becomes reddish brown. The concentrated acid has a great affinity for water, which it absorbs from the atmosphere; and is usefully employed to dry substances placed near it in vacuo. Considerable heat is evolved in its combination with water; when 4 parts by weight of the concentrated acid were suddenly mixed with 1 part of water, the temperature was observed by Dr. Ure to rise to 300° . The density of this acid becomes less in proportion to its dilution.

Acid of sp. gr. 1.78 is a second hydrate, containing two atoms of water to one of acid. This hydrate forms large and regular crystals, even above the freezing point of water, and remains solid, according to Mr. Keir, till the temperature rises to 45° . If the dilute acid is evaporated at a heat not exceeding 400° its water is reduced to the proportion of this hydrate. This second atom of water is expelled by a higher temperature, but the first atom can only be separated from the acid by a stronger base. Sulphuric acid forms still a third hydrate, of sp. gr. 1.632, containing three atoms of water, the proportion to which the water of a more dilute acid is reduced, by evaporation in vacuo at 212° . It is also in the proportions of this hydrate, that the acid and water undergo the greatest condensation, or reduction of volume, in combining. The following then are the formulæ of the definite hydrates of this acid, including that derived by Mitscherlich from the Nordhausen acid:—

HYDRATES OF SULPHURIC ACID.

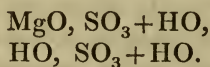
Hydrate in the Nordhausen acid.	.	.	$\text{HO}, 2\text{SO}_3$
Oil of vitriol (sp. gr. 1.850).	.	.	HO, SO_3
Acid of sp. gr. 1.78	.	.	$\text{HO}, \text{SO}_3 + \text{HO}$
Acid of sp. gr. 1.632	.	.	$\text{HO}, \text{SO}_3 + 2\text{HO}$

Sulphuric acid acts in two different modes upon metals, dissolving some, such as copper and mercury, with the evolution of sulphurous acid, and others, such as zinc and iron, with the evolution of hydrogen gas. The metal is oxidated at the expense of the acid itself in the one case, and of the water in combination with the acid in the other. The acid acts with

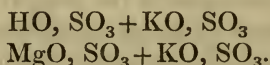
most advantage in the first mode, when concentrated, and in the second when considerably diluted.

The presence of sulphuric acid in a liquid may always be detected by means of chloride of barium, which produces with this acid a white precipitate of sulphate of barytes, insoluble in both acids and alkalies.

Sulphates.—Of no class of salts do chemists possess a more minute knowledge than of the sulphates. The sulphates of zinc, magnesia and other members of the magnesian family correspond closely with the hydrate of sulphuric acid. Thus of the seven atoms of water which the crystallized sulphate of magnesia possesses, it retains one at 400°, and is then analogous to the sulphate of water of sp. gr. 1.78; the formula of these two salts being,



and the atom of water in both salts may be replaced by sulphate of potash, when the sulphate of water forms the salt called the bisulphate of potash, and the sulphate of magnesia forms the double sulphate of magnesia and potash, of which the formulæ also correspond :—



In all these sulphates, there is one atom of acid to one of base. But with potash, sulphuric acid forms a second salt, in which two of acid are combined with one of base, and which has lately been obtained in a crystallized state by M. Jacquelin.* The sulphates are known to correspond with the chromates, and this new salt corresponds with red chromate or bichromate of potash. A third sulphate of potash is to be looked for, corresponding with the terchromate of potash. The series of *anhydrous* sulphates of potash, admitting the latter, will therefore be

	I.	II.	III.
Sulphate of potash	$\text{KO} + \text{SO}_3$	$\text{KO} + \text{SO}_3$	$\text{K} + \text{SO}_4$
Bisulphate of potash	$\text{KO} + 2\text{SO}_3$	$\text{KO} + \text{S}_2\text{O}_6$	$\text{K} + \text{S}_2\text{O}_7$
Tersulphate of potash	$\text{KO} + 3\text{SO}_3$	$\text{KO} + \text{S}_3\text{O}_9$	$\text{K} + \text{S}_3\text{O}_{10}$

* An. de Ch. et de Ph. t. 70, p. 311.

Sulphuric acid appears by the first column to be capable of combining with a base in three multiple proportions, and so also does chromic and probably also manganic and selenic acids which are isomorphous with sulphuric acid, while nitric acid and carbonic acid, so far as is known, combine with bases only in one proportion. Iodic acid, it will afterwards be found, corresponds with sulphuric acid in this respect, there being an anhydrous iodate, biniodate and teriodate of soda (Mr. Penny). The composition of such salts is not easily reconciled with the doctrine of the constitutional neutrality of salts, or with the salt-radical theory, as has already been remarked (page 170). In the second column these sulphates are represented in a different manner, suggested by the relation in composition to each other of certain organic acids, particularly of the class including cyanic, fulminic and cyanuric acids, in the second and third of which, respectively, the atom of cyanogen is doubled and trebled.* A similar duplication and triplication of the atom in compounds, seems to be not an uncommon cause of isomerism, as in the hydrocarburets (page 156, and table of densities, page 134). The acid itself is supposed in the second column to be different in these three salts, namely SO_3 , S_2O_6 , S_3O_9 , and the salts cease to be anomalous, being all represented as neutral salts, containing one atom of acid, to one of base. In the third column, the same view of the constitution of these sulphates is accommodated to the salt-radical theory.

These duplicated and triplicated sulphuric acids are supposed above, to form each a monobasic class of sulphates; but if, moreover, it be assumed that one of them, the duplicated sulphuric acid S_2O_6 , with the corresponding chromic acid Cr_2O_6 , is also capable of forming a bibasic class of salts, then some other salts of the same class will be brought more in accordance with the general views entertained respecting salts, than those salts at present are, as their constitution is generally represented. The salts named will be represented as follows :

† I may take this opportunity to rectify the statement made respecting these acids at page 168. Liebig in his recent memoir on the organic acids has represented cyanic acid as monobasic, $\text{MO} + \text{CN}_2\text{O}$; fulminic as bibasic, $2\text{MO} + \text{C}_2\text{N}_4\text{O}_2$; and cyanuric as tribasic, $3\text{MO} + \text{C}_3\text{N}_6\text{O}_3$, and not these acids as all equally tribasic. *An. de Ch. et de Ph.* t. 63, p. 5.

Gypsum, or hydrated sulphate of lime $2\text{CaO}, \text{S}_2\text{O}_6 + \text{HO} + 3\text{HO}$

Johnston's hydrated sulphate of lime $2\text{CaO}, \text{S}_2\text{O}_6 + \text{HO}$

Glauberite (sulphate of soda and lime) $\left. \begin{array}{c} \text{NaO} \\ \text{CaO} \end{array} \right\} + \text{S}_2\text{O}_6$

Chromate of potash and soda $\left. \begin{array}{c} \text{KO} \\ \text{NaO} \end{array} \right\} + \text{Cr}_2\text{O}_6$

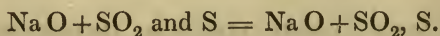
Uses.—Sulphuric acid is employed to a large extent in eliminating nitric acid from nitrate of potash, and in the preparation of hydrochloric acid and chlorine, from chloride of sodium, and also in the processes of bleaching. But the greatest consumption of this acid is in the formation of sulphates, particularly of sulphate of soda, by the decomposition of which salt, nearly all the carbonate of soda of commerce is at present procured.

HYPOSULPHUROUS ACID.

Eq. 602.34 ; S_2O_2 or $\text{SO}_2 + \text{S}$; not isolable.

The hyposulphites are better known than hyposulphurous acid itself, which is a body of little stability, quickly undergoing decomposition, when liberated by a stronger acid from a solution of any of its salts, and resolving itself into sulphurous acid, sulphuretted hydrogen and sulphur. These salts, long considered as a species of double salts, and called *sulphuretted sulphites*, were first supposed to contain a peculiar acid by Dr. Thomson and by Gay-Lussac, a conjecture afterwards verified by Sir John Herschell, whose early researches upon this acid form the subject of a memoir of great interest.*

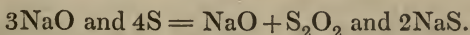
Preparation.—The sulphite of soda, prepared by saturating a solution of carbonate of soda by sulphurous acid (page 319), is converted into hyposulphite, by digesting it upon flowers of sulphur at a high temperature, but without ebullition. The sulphurous acid assumes an atom of sulphur, and remains in combination with the soda; or, in symbols—



The solution may afterwards be evaporated, (ebullition being

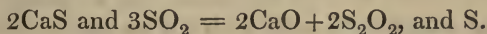
* Edinburgh Philosophical Journal, vol. 1, pp. 8 and 396.

always avoided, as the hyposulphites are all partially decomposed at 212° ;) and affords large crystals of the hyposulphite of soda. When solution of caustic soda is digested upon sulphur, the latter is likewise dissolved, and a mixture of 1 eq. of hyposulphite of soda with 2 eq. of sulphuret of sodium results, of which the last may dissolve an excess of sulphur:—

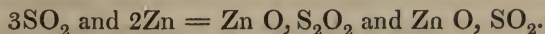


Exposed to the air, this solution slowly absorbs oxygen, and if it contains a certain excess of sulphur, passes entirely into hyposulphite of soda.

The hyposulphite of lime is also formed, by digesting together 1 part of sulphur and 3 of hydrate of lime at a high temperature, when changes of the same nature occur as with sulphur and caustic soda, and the solution becomes red; a stream of sulphurous acid gas is conducted through the solution after it has cooled, and converts the whole salt into hyposulphite, occasioning at the same time a considerable deposition of sulphur. The reaction here is rather complicated, the sulphurous acid uniting with one portion of sulphur, to form hyposulphurous acid, and also liberating another portion of the same element from the sulphuret of calcium. It is expressed in the following formula:



Zinc and iron also dissolve in the solution of sulphurous acid in water, with little or no effervescence, deriving the oxygen necessary to convert them into oxides, not from water, but from the sulphurous acid, two-thirds of which are thereby converted into hyposulphurous acid, which combines with half of the oxide produced; while the other third, remaining as sulphurous acid, unites with the other moiety of the same oxide:—



The hyposulphite obtained by this process is, therefore, mixed with a sulphite.

Properties.—The acid of these salts undergoes decomposition when they are strongly heated, or treated with an acid. It forms soluble salts with lime and strontian, in which respect it differs from sulphurous and sulphuric acids; the hyposulphite of barytes is insoluble. It also forms a remarkable salt with

silver, which has no metallic flavour, but tastes extremely sweet. The existence of a hyposulphite in a solution, is easily recognized, by its possessing the power to dissolve freshly precipitated chloride of silver, and become sweet.

Uses.—The hyposulphite of soda is employed to distinguish between the earths strontian and barytes, the latter of which it precipitates, and not the former. It is also applied, in certain circumstances, to dissolve the insoluble salts of silver.

CHLOROSULPHURIC ACID.

Eq. 843.8 or 67,6; SO_2Cl ; 4652; .

A compound which contains sulphur, oxygen, and chlorine, has lately been discovered by M. Regnault, which he considers as a combination of sulphurous acid with chlorine, and therefore a member of the sulphurous acid series.* The circumstances of the formation of this compound are singular. Chlorine and sulphurous acid gases, dry or humid, may be mixed and even transmitted through a glass tube, containing pounded glass or spongy platinum, at all temperatures, without combining. But when chlorine, which should be perfectly dry, is allowed to meet in a glass balloon at once sulphurous acid and olefiant gas, perfectly dry, a chloride of sulphurous acid, and a chloride of olefiant gas are simultaneously formed, with the evolution of much heat, and condense together as an extremely mobile liquid, of a sharp and suffocating odour. Regnault has observed that neither of these compounds can be produced without the other, although they are produced in a variable relation to each other as to quantity. The olefiant gas, evolved upon heating 6 parts of oil of vitriol with 1 part of concentrated alcohol, passed through two vessels containing oil of vitriol, to dry it, contains enough of sulphurous acid for the preceding experiment. The liquor produced, thrown into water, falls first to the bottom, in the form of oily drops, but soon dissolves partially with elevation of temperature, and the chloride of olefiant separates unaltered. The chlorosulphuric acid itself, in dissolving, decomposes 1 atom of water, and changes into hydrochloric acid and sulphuric acid, a reaction which demonstrates the original compound to consist of 1 atom of sulphurous acid with 1 atom of chlorine.

* An. de Ch. et de Ph. t. 69, p. 170.

The density of the vapour of chlorosulphuric acid, was found by experiment to be 4703, which agrees with the theoretical density 4652. It consists of 2 volumes of sulphurous acid and 2 volumes of chlorine condensed into 2 volumes, which form the combining measure of the vapour. In its condensation, it resembles the vapour of anhydrous sulphuric acid. This body also corresponds exactly in composition with the compound hitherto called chlorochromic acid, of which the true formula is $\text{Cr O}_2\text{Cl}$, chromium being substituted in the latter for the sulphur of the former.

With dry ammoniacal gas, chlorosulphuric acid forms a white powder, which is a mixture of the hydrochlorate of ammonia (sal ammoniac) and the true *sulphamide*, $\text{SO}_2 + \text{NH}_2$. It does not combine, as an acid, with bases.

Mr. Lyon Playfair has also lately formed a corresponding *iodosulphuric acid*, by distilling 2 equivalents of iodine with 1 eq. of sulphite of lead, and by transmitting sulphurous acid through a solution of iodine in wood-spirit, in which this compound is soluble. It is a dense liquid, decomposed by water. Mr. Playfair is likely to add other acids to this class.

NITROSULPHURIC ACID.

Eq. 778.2 or 62.3; SNO_4 or SO_2, NO_2 ; not isolable.

Sir H. Davy made the observation that nitric oxide is absorbed by a mixture of sulphite of soda and caustic soda, and that a compound is produced, of which the principal characteristic is to disengage abundance of nitrous oxide, upon the addition of an acid to it. He concluded that the nitrous oxide, which then escapes, was previously united with soda, and gave this as an instance of the combination of that neutral oxide with an alkali. As the sulphite of soda became at the same time sulphate, the conversion of the nitric oxide into nitrous oxide appeared to be explained. It has, however, been lately proved by Pelouze, that a new acid is formed in the circumstances of the experiment, to which he has given the name nitrosulphuric, and which may be considered a compound of sulphurous acid and nitric oxide, or another member of the sulphurous acid series.*

* Pelouze in Taylor's Scientific Memoirs, vol. 1, p. 470; or An. de Ch. et de Ph. t. 60, p. 151.

Preparation.—If a mixture be made over mercury of 2 volumes of sulphurous acid, and 4 volumes of nitric oxide, which are combining measures of these gases, no change occurs; but on throwing up a strong solution of caustic potash into the gases, they disappear entirely after some hours, combining with a single equivalent of potash, and forming together the nitrosulphate of potash. But it is better to prepare the nitrosulphate of ammonia. A concentrated solution is made of sulphite of ammonia, which is mixed with 5 or 6 times its volume of solution of ammonia, and into this, nitric oxide is passed for several hours. A number of beautiful crystals are gradually deposited; they are to be washed with a solution of ammonia previously cooled, which besides the advantage of retarding their decomposition, offers that of dissolving less of them than pure water. When the crystals are desiccated, they should be introduced into a well closed bottle; in this state they undergo no alteration. The same process is applicable to the corresponding salts of potash and soda. When a strong acid is added to a solution of these salts, for the purpose of isolating the nitrosulphuric acid, the latter on being set free, decomposes spontaneously into sulphuric acid and nitrous oxide, which comes off with effervescence.

Properties.—The acid of the nitrosulphates is not precipitated by barytes. The nitrosulphate of potash, when heated, becomes sulphite, and evolves nitric oxide; but the salts of soda and ammonia become sulphates, and evolve nitrous oxide. No nitrosulphates of the metallic oxides which are insoluble in water, have been formed, or appear capable of existing; for when such salts as chloride of mercury, the sulphate of zinc or of copper, the persulphate of iron and the nitrate of silver are added to the nitrosulphate of ammonia, they produce a brisk effervescence of nitrous oxide, with the formation of sulphate of ammonia, or they decompose the nitrosulphate of ammonia as free acids do. Indeed the only nitrosulphates which have been formed are those of potash, soda and ammonia. These are neutral, and have a sharp and slightly bitter taste, with nothing of that of the sulphites.

These salts vie with the peroxide of hydrogen in facility of decomposition. The nitrosulphate of ammonia resists 230° , but is decomposed with explosion a few degrees above that temperature, caused by the rapid disengagement of nitrous oxide.

Solutions of the nitrosulphates are not stable above the freezing point, but their stability is much increased by an excess of alkali. They are resolved into sulphate and nitrous oxide, by the mere contact of certain substances, which do not themselves undergo any change, such as spongy platinum, silver and its oxide, charcoal powder and peroxide of manganese, by acids, even carbonic acid, and by metallic salts.

HYPOSULPHURIC ACID.

Eg. 902.3 or 72.24.; $S_2 O_5$; not isolable.

Preparation.—This acid of sulphur was discovered by Gay-Lussac and Welter, in 1819. To prepare it, a quantity of peroxide of manganese, which must not be hydrated, is reduced to an extremely fine powder, suspended by agitation in water, and sulphurous acid gas is transmitted through the water. The temperature is apt to rise during the absorption of the gas, but must be repressed, otherwise much sulphuric acid is produced, the formation of which, indeed, it is impossible to prevent entirely, but of which the quantity is reduced almost to nothing, when the liquor is kept cold during the operation. The peroxide of manganese disappears, and a solution of hyposulphate of the protoxide of manganese is formed; 2 equivalents of sulphurous acid, and 1 of peroxide of manganese, forming one of hyposulphuric acid and one of protoxide of manganese, or



The solution is filtered, and then mixed with a solution of sulphuret of barium, which occasions the precipitation of the insoluble sulphuret of manganese, with the transference of the hyposulphuric acid to barytes. From this hyposulphate of barytes, the hyposulphates of other metallic oxides may be prepared, by adding their sulphates to that salt, when the insoluble sulphate of barytes will precipitate, and the hyposulphate of the metallic oxide added remain in solution. But to procure the hyposulphuric acid itself, the solution of hyposulphate of barytes may be evaporated to dryness, and being perfectly pure, it is reduced to a fine powder, weighed and dissolved in water; for 100 parts of it 18.78 parts of oil of vitriol are taken, which after dilution with 3 or 4 times as much water, are employed to decompose the salt of barytes. The liberated hyposulphuric

acid solution is filtered, and evaporated in vacuo over sulphuric acid, till it attains a density of 1.347, which must not be exceeded, as the acid solution begins then to decompose spontaneously into sulphurous acid, which escapes, and sulphuric acid which remains in the liquor.

Properties.—This acid has not been obtained in the anhydrous condition. Its aqueous solution has no great stability, being decomposed at its temperature of ebullition. The same solution exposed to air in the cold slowly absorbs oxygen, according to Heeren, and becomes sulphuric acid. But neither nitric acid, nor chlorine, nor peroxide of manganese oxidize this acid, unless they are boiled in its solution. Its salts are perfectly stable, either when in solution, or when dry, and are in general very soluble, having some analogy to the nitrates. A hyposulphite, when heated to redness, leaves a neutral sulphate, and allows a quantity of sulphurous acid to escape, which would be sufficient to form a neutral sulphite with the base of the sulphate. This class of salts was particularly examined by Heeren.* Hyposulphuric acid is imagined to exist in acid compounds produced by the action of sulphuric acid on some principles of organic chemistry, in the sulpho-napthalic acid, for instance.

SECTION VIII.

SELENIUM.

Eq. 494.58 or 39.63 ; Se ; *density of vapour unknown.*

This element was discovered by Berzelius in 1817, in the sulphur of Fahlun, employed in a sulphuric acid manufactory in Sweden, and was named by him selenium, from Σελήνη, the moon, on account of its strong analogy to another element tellurium, which derives its name from *tellus*, the earth. It is one of the least abundant of the elements, but is found in minute quantity in several ores of copper, silver, lead, bismuth, tellurium and gold in Sweden and Norway ; and in combination with lead, silver, copper and mercury in the Hartz. It is extracted from a seleniferous ore of silver of a mine in the latter district, and supplied for sale in little cylinders of the thickness of a goose-quill, and three inches in length ; or in the form of small medal-

* Poggendorff's Annalen, v. vii, p 77.

lions of its discoverer. It has also been found in the Lipari islands in combination with sulphur, and can sometimes be detected in the sulphuric acid, both of Germany and England. It is separated from its combinations with sulphur and metals by a very complicated process, for which I must refer to the works of Berzelius.*

Properties of selenium.—This element is allied to sulphur, and like that body, exhibits considerable variety in its physical characters. When it cools after being distilled, its surface reflects light like a mirror, has a deep reddish brown colour, with a metallic lustre resembling that of polished blood-stone. Its density is between 4.3 and 4.32. When cooled slowly after fusion, its surface is rough, of a leaden grey colour, its fracture fine-grained, and the mass resembles exactly a fragment of cobalt. But as selenium does not conduct electricity, and its metallic characters are not constant, it is better classed with the non-metallic bodies. Its powder is of a deep red colour. By heat it is softened, becoming semifluid at 212° , and fusing completely a few degrees higher. It remains a long time soft on cooling, and may then be drawn out like sealing wax into thin and very flexible threads, which are grey and exhibit a metallic lustre by reflected light, but are transparent and of a ruby red colour by transmitted light. It boils about 650° , and gives a vapour of a yellow colour, less intense than that of sulphur, but more so than that of chlorine. The density of this vapour has not been ascertained.

Selenium combines in three proportions with oxygen, forming selenic acid, which corresponds with sulphuric acid, selenious acid corresponding with sulphurous acid, and a protoxide, to which there is no oxide of sulphur analogous.

Oxide of selenium, SeO .—This is a colourless gas, sparingly soluble in water, formed when selenium is heated in air without burning freely. It has a powerful odour, suggesting that of decaying horse-radish, by means of which the smallest trace of selenium may be detected in minerals, when heated before the blow-pipe, this gas being then formed.

Selenious acid, SeO_2 .—Selenium strongly heated in a glass bulb, with a current of oxygen passing over it, takes fire and

* Annals of Philosophy, vol. 13, p. 401; or An. de Ch. et de Ph. t. 9, p. 160; also Berzelius's *Traité*, t. 1, p. 334, Brussels edition, 1838.

burns with a flame, white at the base, and of a bluish green at the point and edges, but not strongly luminous; selenious acid at the same time condenses as a white sublimate, in long quadrilateral needles. Its vapour has the colour of chlorine. The same acid is the sole product of the action of nitric or nitromuriatic acid upon selenium, and is obtained on slowly cooling the liquor, in large prismatic crystals, striated lengthwise, which have a considerable resemblance to nitre. These crystals are hydrated selenious acid. This acid is largely soluble, both in water and alcohol. It is decomposed when in solution and selenium precipitated by zinc, iron or sulphite of ammonia, with the assistance of a free acid. The selenite of ammonia is also decomposed by heat and leaves selenium. The selenious is a strong acid, displacing nitric and hydrochloric acids from their combinations, but is displaced in its turn by the more fixed acids, sulphuric, boracic, &c.

Selenic acid, SeO_3 .—Selenium is brought to this superior state of oxidation at a high temperature, by fusion with nitre, a process which affords the seleniate of potash. The selenic acid is precipitated from that salt by the nitrate of lead; and the insoluble seleniate of lead, after being washed, is diffused through water and decomposed by a stream of sulphuretted hydrogen gas, which converts the lead into insoluble sulphuret of lead and liberates selenic acid. A solution of this acid may be concentrated till its boiling point rises to 536° , but above that temperature it changes rapidly into selenious acid, with disengagement of oxygen. Its density is then 2.60, and it contains little more than a single equivalent of water, and therefore corresponds with the protohydrate of sulphuric acid, or oil of vitriol. Selenic acid has never been obtained in the anhydrous condition. Zinc and iron are dissolved by this acid, with the evolution of hydrogen gas; and with the aid of heat it dissolves copper and even gold, an operation in which it is partially converted into selenious acid. But it does not dissolve platinum. To precipitate its selenium, the acid may be digested with hydrochloric acid, which occasions the formation of selenious acid and the evolution of chlorine, and then sulphurous acid throws down the selenium. The compounds of selenic acid with bases, so much resemble the corresponding sulphates, in their crystalline form, colour and external characters, that they can only be distinguished from them by the property which

the seleniates have of detonating when ignited with charcoal, and causing a disengagement of chlorine when heated with hydrochloric acid. To separate the selenic from the sulphuric acid, Berzelius recommends the saturation of the acids with potash, and the ignition of the dried salt, mixed with salamoniac; the selenic acid is decomposed by the ammonia and reduced to the state of selenium.

SECTION XI.

PHOSPHORUS.

Eq. 392.28 or 31.44 (196.14 or 15.72 according to Berzelius and Turner;) density of vapour 4327; \square .

This remarkable element appears to be essential to the organization of the higher animals, being found in their fluids, and forming in the state of phosphate of lime, the basis of the solid structure of the bones. It is also found in most plants, and in a few minerals. Phosphorus was first obtained by Brand of Hamburgh in 1660, but Kunkel first made public a process for preparing it, which was afterwards improved by Margraff and by Scheele. Its ready inflammability, from which phosphorus derived its name, has always made this substance an object of popular interest; while the singularity, importance and variety of the phosphoric compounds have drawn to them no ordinary share of the attention of chemists.

Preparation.—Phosphorus is not a substance that can be easily prepared on a small scale, but ever since the time of Godfrey Hankwitz, to whom Mr. Boyle communicated a process for preparing it, phosphorus has been manufactured in London, in considerable quantity and of great purity, for the use of chemists. The earth of bones is decomposed by 2-3rds of its weight of sulphuric acid, and the insoluble sulphate of lime separated by filtration from the soluble phosphoric acid, which passes through with a quantity of phosphate of lime in solution. The acid liquor is then evaporated to the consistence of a syrup, and mixed with charcoal to form a soft paste, which is rubbed well in a mortar, and then dried in an iron pot with constant stirring till the mass begins to be red hot. It is allowed to cool, and introduced as rapidly as possible into a stone-

ware retort, previously covered with a coating of fire clay. The beak of the retort is inserted into a wider copper tube of a few feet in length, the free end of which is bent downwards a few inches from its extremity; and the descending portion introduced into a wide-mouthed bottle, containing enough of water to cover the extremity of the tube to the extent of a line or two. The heat of the furnace in which the retort is placed, is slowly raised for three or four hours, and then urged vigorously till phosphorus ceases to drop into the water from the copper tube, which may continue from fifteen to thirty hours, according to the size of the retort. Carbon at a high temperature takes oxygen from the phosphoric acid, and becomes carbonic oxide, so that the phosphorus is all along accompanied by that gas.

Wöhler recommends, instead of the preceding process, to calcine ivory black, which is a mixture of phosphate of lime and charcoal, with fine quartz sand and a little more ordinary charcoal, in cylinders of fire clay, at a very high temperature. Each cylinder has a bent copper tube adapted to it, one branch of which descends into a vessel containing water. The efficiency of Wöhler's process depends upon the silica acting as an acid, and combining with the lime of the phosphate, at a high temperature, while the liberated phosphoric acid is decomposed by the carbon.

Properties.—At the usual temperature phosphorus is a translucent soft solid of a light amber colour, which may be bent or cut with a knife, and the cut surface has a waxy lustre. Its density is 1.77. Phosphorus melts at 108° , undergoing a remarkable dilatation of 0.0314 of its volume and becoming transparent and colourless immediately before fusion. It forms a transparent liquid, possessing like most combustible bodies, a high refracting power. At 217° it begins to emit a slight vapour, and boils at 550° , being converted into a vapour which is colourless, of sp. gr. 4355, according to the experiment of Dumas, which coincides almost with the theoretical density 4327. Its combining measure, like that of oxygen, is 1 volume, allowing its equivalent to be 392. When fused and left undisturbed, it sometimes remains liquid for hours at the usual temperature, particularly when covered by an alkaline liquid, but becomes solid when touched. Thenard has observed that when cooled very suddenly, as by throwing it melted into ice-cold water, it becomes absolutely black. Light causes it, in

all circumstances, to assume a red tint; to avoid which action phosphorus is usually preserved in an opaque bottle. From its solution in hot naphtha it may be obtained, in cooling, in regular dodekahedral crystals. It is quite insoluble in water, but soluble to a small extent, with the aid of heat, in fixed and volatile oils, in sulphuret of carbon, of which 100 parts dissolve 20 of phosphorus, in chloride of sulphur, sulphuret of phosphorus, and ether.

Phosphorus undergoes oxidation in the open air, and diffuses white vapours, which have a peculiar odour, suggesting to some that of garlic, and are luminous in the dark; and at the same time the phosphorus becomes covered with acid drops, which arise from the phosphorous acid, produced in these circumstances, attracting the humidity of the air. This slow combustion is attended with a sensible evolution of heat, and may terminate in the fusion of the phosphorus, and its inflammation with combustion at a high temperature. There is a necessity for caution, therefore in handling phosphorus, a burn from this body in a state of ignition being in general exceedingly severe. It is preserved under the surface of water. The low combustion of phosphorus has been particularly studied. It is not observed a few degrees below 32° , but is sensible at that temperature, and increases perceptibly a few degrees above it. The presence of certain gaseous substances, even in minute quantity, has a remarkable effect in preventing the slow combustion of phosphorus; thus at 66° , it is entirely prevented by the presence,

	Volumes of Air.
of 1 volume of olefiant gas in	450
of 1 volume of vapour of sulphuric ether in. . . .	150
of 1 volume of vapour of naphtha in. . . .	1820
of 1 volume of vapour of oil of turpentine in. . . .	4444

and the influence of these gases or vapours is not confined to low temperatures, a certain admixture of all of them defending phosphorus from oxidation even at 200° . But on allowing such a gaseous mixture to expand, by diminishing the pressure upon it to a half or a tenth, the phosphorus becomes luminous, and the proportion of foreign gas required to prevent the slow combustion must be greatly increased. The only explanation of this phenomenon, which can be offered at present, is that the gases which exert this influence have an attraction for oxygen,

and there is reason to believe are themselves undergoing a slow oxidation at the same time. Now when two oxidable bodies are in contact, one of them often takes precedence in combining with oxygen, to the entire exclusion of the other. Potassium is defended from oxidation in air, by the same vapours, although to a less degree.* It is curious that in pure oxygen, phosphorus may remain without oxidating at all, at temperatures below 60° , but an inconsiderable rarefaction of the gas, from diminution of the pressure upon it, will cause the phosphorus to burst into the luminous condition. The dilution of the oxygen with nitrogen, hydrogen or carbonic acid produces the same effect. When gradually heated in air, phosphorus generally catches fire, and begins to undergo the high combustion, before its temperature has risen to 140° ; of this high combustion, the sole product is phosphoric acid.

Phosphorus is susceptible of four different degrees of oxidation, the highest of which is a powerful acid, while the acid character is not absent even in the lowest. These compounds are:

Oxide of phosphorus.	.	.	$2P + O$
Hypophosphorous acid.	.	.	$P + O$
Phosphorous acid	.	.	$P + 3O$
Phosphoric acid.	.	.	$P + 5O$.

OXIDE OF PHOSPHORUS.

Eq. 884.56 or 70.88; P_2O .

When burned in air or oxygen, phosphorus generally leaves behind it a small quantity of a red matter, which is an oxide of phosphorus. The same compound is obtained, in larger quantity, by directing a stream of oxygen gas, upon melted phosphorus, under hot water, and was found by Pelouze to contain 3 equivalents of phosphorus to 2 of oxygen.†

But this oxide is impure, and the definite oxide appears to have been first obtained by Leverrier, who has carefully examined it.‡ His process is to expose to the air small fragments

* Quarterly Journal of Science, N.S. vol vi. p. 83.

† An. de Ch. et de Ph. t. 50, p. 83.

‡ An. de Ch. et de Ph. t. 65, p. 257.

of phosphorus covered by the liquid chloride of phosphorus (PCl_3), in an open bolt-head. Phosphoric acid is formed, and also a yellow matter, which he finds to be a phosphate of the oxide of phosphorus, and which gives a yellow solution with water. This solution is decomposed about 176° , and a flocculent yellow matter subsides, which is a hydrate of the oxide of phosphorus, nearly insoluble in water. This compound abandons its combined water, when dried in vacuo over sulphuric acid, or when cooled below 32° , when the water separates as ice, and oxide of phosphorus remains perfectly pure.

The oxide of phosphorus is a powder of a canary yellow colour, denser than water, and soluble neither in water, alcohol, nor ether. It may be kept in dry air without change. It resists a temperature of 570° without decomposition, but assumes a lively red colour; and does not take fire in air till heated a little above the boiling point of mercury. This oxide absorbs dry ammoniacal gas, and appears to form feeble combinations with the fixed alkalies. Leverrier assigns to its hydrate the composition $\text{P}_2\text{O} + 2\text{HO}$, and to its phosphate, $2\text{P}_2\text{O} + 3\text{PO}_5$.

HYPOPHOSPHOROUS ACID.

Eq. 492.28 or 39.44; PO; not isolable.

This acid was discovered in 1816 by Dulong.* It was obtained by the action of water upon the phosphuret of barium, of which the phosphorus of one portion oxidates and becomes the acid in question, at the expense of the water, while the phosphorus of another portion, combining with the hydrogen of the water, produces phosphuretted hydrogen gas. Rose prepares the same hypophosphite of barytes, by boiling phosphorus and caustic barytes together, till all the phosphorus disappears and the vapours have no longer the smell of garlic.† This solution is filtered, and to separate the hypophosphorous acid from barytes, diluted sulphuric acid is added which precipitates the latter. The acid remaining in solution may be concentrated with caution, to the consistence of a thick syrup, but affords no crystals. More strongly heated, this hydrate of

* An. de Ch. et de Ph. t. 2. p. 141.

† H. Rose, sur les Hypophosphites, An. de Ch. et de Ph. t. 38, p. 258.

hypophosphorous acid undergoes decomposition, being converted into phosphoric acid, with the evolution of phosphuretted hydrogen and a deposition of phosphorus (Dulong).

The hypophosphites are all soluble in water, and like the salts of the magnesian family, such as those of magnesia and cobalt, easily crystallized. The dry salts are permanent in the air, but their solutions evaporated by heat, absorb oxygen. They contain $1\frac{1}{2}$ equivalents of water, which are essential to their constitution (Rose).

Considering the disposition of the acids of phosphorus to be bibasic and tribasic, it is not impossible that the real equivalent of this acid may be either $2P+2O$, like hyposulphurous acid, or $3P+3O$, instead of PO . The subject requires farther investigation.

PHOSPHOROUS ACID.

Eq. 692.28, or 55.44; PO_3 .

Preparation.—This acid is the principal product of the slow combustion of phosphorus, but changes after its formation into phosphoric acid, from the absorption of oxygen. It may be obtained in the anhydrous condition by burning phosphorus with imperfect access of air. Berzelius recommends for this operation a tube of glass, about 10 inches in length and $\frac{1}{2}$ inch in diameter, which is nearly closed at one end, an opening no greater than a large pin hole being left there, and at a distance of an inch from this extremity the tube is bent at an obtuse angle. A small fragment of phosphorus is introduced into the angle of the tube, and heated till it takes fire. It burns with a pale greenish flame, and the phosphorous acid produced is carried along by the feeble current of air, and condenses in the ascending part of the tube, as a white powder, not in the slightest degree crystalline. The phosphorus must not be so much heated as to cause it to sublime unchanged. In contact with air, phosphorous acid is apt to inflame, from the heat occasioned by the condensation of moisture, and is converted into phosphoric acid. The phosphorous acid itself is immediately soluble in water, while the phosphoric acid, which it sometimes contains, remains for a short time undissolved, in the form of white translucent flocks.

Hydrated phosphorous acid, which is the source of pure

phosphuretted hydrogen gas, cannot be obtained without some trouble. When a few drops of water are thrown on the chloride of phosphorus (PCl_3) that compound evolves hydrochloric acid gas, and gives hydrated phosphorous acid. But it is more conveniently obtained by the method of Droquet. Two or three ounces of phosphorus are melted in a cylindrical glass receiver or sealed tube, of 8 or 10 inches in length and nearly an inch in diameter, and the tube nearly filled with water. This tube, which will contain a column of fluid phosphorus of 5 or 6 inches in height is then properly disposed in a bason or bolt-head of warm water, so as to retain the phosphorus fluid. Chlorine gas is conveyed by a quill tube, from the flask in which it is generated, to the bottom of the fluid phosphorus, where combination takes place with ignition, and the chloride of phosphorus is formed. This chloride is dissolved by the water covering the phosphorus, and converted into hydrochloric acid and phosphorous acid. The chlorine must be transmitted very slowly through the phosphorus, as any portion of that gas which reaches the water, converts the phosphorous into phosphoric acid; and the absorption of the chlorine by the phosphorus is most complete, when it is free from any other gas. When the remaining phosphorus fixes, upon cooling, the acid fluid may be poured off, and concentrated by boiling, till it becomes syrupy and the volatile hydrochloric acid is entirely expelled. Phosphuretted hydrogen may also be obtained from the iodide of phosphorus, which is more easily prepared.

Properties.—In its most concentrated state, the hydrate of phosphorous acid contains three equivalents of water, its formula being $3\text{HO} + \text{PO}_3$; and when heated it is resolved into hydrated phosphoric acid, and pure phosphuretted hydrogen gas, which is not spontaneously inflammable. The solution of phosphorous acid absorbs oxygen from the air, slowly, if concentrated, but quickly when dilute. Like sulphurous acid, it takes oxygen from the salts of mercury and the less oxidable metals, and precipitates the latter, particularly when aided by heat. It is one of the feeblest acids known.

Phosphites.—The class of phosphites, which has been examined is certainly tribasic, that is, they contain 3 atoms of base to 1 of phosphorous acid. The hydrated acid is the tribasic phosphite of water. All our information respecting them is contained in the papers of Berzelius.*

* An. de Ch. et de Ph. t. 2, pp. 151, 217, 329; and 10, p. 278.

PHOSPHORIC ACID.

Eg. 892.28, or 71.44; PO_5 ; forms three hydrates and three classes of salts :

<i>Monobasic phosphate of water, or metaphosphate of water</i>	$\text{HO} + \text{PO}_5$
<i>Bibasic phosphate of water, or pyrophosphate of water.</i>	$2\text{HO} + \text{PO}_5$
<i>Tribasic phosphate of water, or phosphate of water</i>	$3\text{HO} + \text{PO}_5$

Preparation.—To obtain this acid in a state of purity, the most convenient process is to set fire to about a drachm of phosphorus upon a little metallic capsule, placed in the centre of a large stone-ware plate, and immediately cover it by a dry bell jar of the largest size. The phosphorus is converted into white flakes of phosphoric acid which are retained, with very little loss, within the bell-jar, and fall upon the plate like snow. The dry phosphoric acid is distinguished by the same shade of white, absence of crystallization, and perfect opacity, as solid carbonic acid. Exposed for a few minutes to the air, it deliquesces; and when the solid acid is collected in a wine-glass, and a few drops of water are thrown upon it, it is converted into a hydrate with explosive ebullition, from the heat evolved. The anhydrous acid is perfectly fixed, unless in the presence of aqueous vapour, when it sublimes away, probably in the state of a hydrate.

Phosphorus may likewise be oxidated by means of nitric acid. In this operation, the fuming nitric acid should be diluted with an equal bulk of water, to avoid accidents from the violent action of the acid, which may cause the phosphorus to be projected in a state of ignition; the diluted acid is boiled upon the phosphorus, and being afterwards evaporated to dryness, it yields a hydrated phosphoric acid.

Phosphoric acid is also obtained in large quantity from calcined bones, which are reduced to a fine powder and mixed with 4-5ths of their weight of oil of vitriol, previously diluted with 4 or 5 times its bulk of water, as in the preparation of phosphorus (page 339). Carbonate of ammonia is then added to the filtered solution of phosphoric acid and the resulting phosphate of ammonia being evaporated to dryness and heated to low redness in a platinum crucible, a hydrated phosphoric

acid remains, in a fused state, which is known as glacial phosphoric acid, from its resemblance to ice.

To exhibit many of its properties phosphoric acid must be first dissolved in water, when the compound will be found to be marked by an inconstancy and variableness in its characters, most unusual in a strong acid. This arises from the circumstance that it is not actual phosphoric acid which dissolves in water, any more than it is true sulphuric acid, which dissolves in water, when oil of vitriol is added to that fluid. It is a hydrate of both acids, which is soluble; the phosphate of water in the one case and the sulphate of water in the other. But the phosphoric acid differs from the sulphuric, in a singular and almost peculiar capacity to form three different salts of water, instead of one only; and these three phosphates of water are all soluble without change, and exhibit properties so different that they might be supposed to contain three different acids. When the dry acid from the combustion of phosphorus is thrown into water, it produces a mixture, in variable proportions, of the three hydrates; but each of them may be had separately and in a state of purity by a particular process.

Terhydrate, or tribasic phosphate of water, $3\text{HO} + \text{PO}_5$.—The common phosphate of soda of pharmacy may be had recourse to for all the hydrates of phosphoric acid; but it should be first dissolved and crystallized anew to purify it. To a warm solution of the pure phosphate of soda in a bason, add a solution of acetate of lead in distilled water, so long as it occasions a precipitate; the phosphate of soda requires rather more than an equal weight of acetate of lead. The dense insoluble phosphate of lead, which precipitates, is washed, and being afterwards suspended in cold water, is decomposed by a stream of sulphuretted hydrogen gas sent through it. The liquor may then be warmed, to expel the excess of sulphuretted hydrogen, and filtered from the black sulphuret of lead: it is very sour, and contains the terhydrate of phosphoric acid. The characters of this acid solution are, to give a yellow precipitate with nitrate of silver, to yield the common phosphate of soda when neutralized with carbonate of soda, to form salts which have invariably 3 atoms of base to 1 of phosphoric acid, and to be unalterable by boiling its solution or keeping it for any length of time. The class of salts which this hydrate forms are the old phosphates, which have been long known, and it is convenient to allow them to be particu-

larly distinguished as the phosphates or the common phosphates.

Deuto-hydrate of phosphoric acid, or bibasic phosphate of water, $2\text{HO} + \text{PO}_5$.—Dr. Clark first discovered that when the phosphate of soda is heated to redness, it is completely changed, and after being dissolved in water affords crystals of a new salt, which he named the pyrophosphate of soda, an observation which led to the most important results.* If a solution of this salt, which it is not necessary to crystallize, be precipitated by acetate of lead, the insoluble salt of lead washed and decomposed by sulphuretted hydrogen, as before, an acid liquor is obtained which contains the deuto-hydrate of phosphoric acid. It must not be warmed to expel the excess of sulphuretted hydrogen, but be left in a shallow bason for 24 hours to permit the escape of that gas. This acid, when neutralized with carbonate of soda, gives Dr. Clark's pyrophosphate of soda. It also gives a white precipitate with nitrate of silver; all the salts which it forms, have uniformly two atoms of base. Their trivial name is the *pyrophosphates*, and since that term has come into general use, it is not likely to be superseded by the systematic, but rather cumbrous designation of bibasic phosphates. A dilute solution of the deuto-hydrate of phosphoric acid may be preserved for many months without change, but when the solution is exposed for some time to a high temperature, it passes entirely into the terhydrate.

Protohydrate of phosphoric acid.—If the biphosphate of soda be heated to redness, a salt is formed, which treated in a similar manner with the last, gives an acid liquor, containing the protohydrate of phosphoric acid. To prepare the biphosphate itself, a solution of the terhydrate of phosphoric acid is added to a solution of common phosphate of soda, till it is found that a drop of the latter is no longer precipitated by chloride of barium. The biphosphate of soda, which is now in solution, can only be crystallized in cold weather. The glacial phosphoric acid also, is in general almost entirely the protohydrate. This hydrate is characterized by producing a white precipitate in solution of albumen, and in solutions of the salts of earths and metallic oxides precipitates which are remarkable semifluid

* Edinburgh Journal of Science, vol. VII p. 298, (1826) ; or An. de Ch. et de Ph. t. 41. p. 276.

bodies, or soft solids, without crystallization. All these salts contain only one atom of base to one of acid, like the protohydrate of the acid itself. The trivial name *metaphosphates* was applied to the class by myself, to mark the cause of the retention of peculiar properties by their acid, when free and in solution, namely that it was not then simply phosphoric acid, but phosphoric acid *together with* water.* This is the least stable of the hydrates of phosphoric acid being converted rapidly, by the ebullition of its solution, into the terhydrate. If the terms *metaphosphoric acid* and *pyrophosphoric acid* are employed at all, it is to be remembered that they are applicable to the proto and deutohydrates, and not to the acid itself, which is the same in all the hydrates. But to prevent the chance of misconception, metaphosphate of water and pyrophosphate of water might be substituted for these terms.

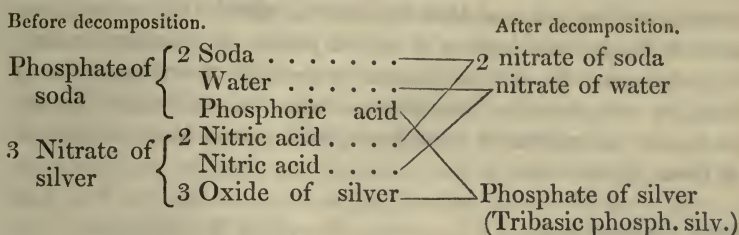
A solution of the terhydrate of phosphoric acid, evaporated in vacuo over sulphuric acid, crystallizes in thin plates, which are extremely deliquescent. When heated to 400°, that hydrate loses a portion of water, and becomes a mixture of the deuto and protohydrates; and by heating it to redness for some time, the proportion of water may be reduced to one equivalent, or perhaps even less than this. But at that high temperature much of the hydrated phosphoric acid passes off in vapour. The solution of phosphoric acid is not poisonous, nor when concentrated does it act as a caustic, but it injures the teeth from its property of dissolving phosphate of lime. A solution of the latter salt in phosphoric acid has been prescribed in rickets, a disease which indicates a deficiency of earthy phosphates in the system. The phosphate of soda also is administered as a mild aperient; its taste is saline, but not disagreeably bitter.

Phosphates.—The formation of three classes of phosphates from the three basic hydrates of phosphoric acid, affords an excellent illustration of the formation of compounds by substitution. The quantity of fixed base, such as soda, with which phosphoric acid combines in the humid way, being entirely regulated by the proportion of water previously in union with the acid, which is simply replaced by the fixed base. Thus, the

* Researches on the arseniates, phosphates and modifications of phosphoric acid. Phil. Trans. 1833, p. 253; or Phil. Mag. 3rd series, vol. 4, p. 401.

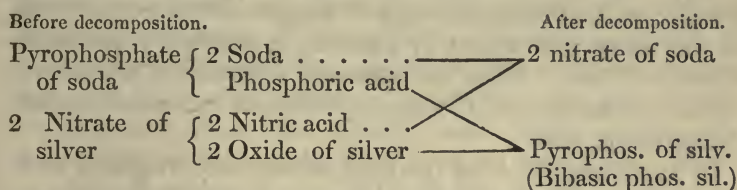
protohydrate of phosphoric acid combines with no more than one, and the deutohydrate with no more than two proportions of soda, although three or a larger number of proportions of alkali be added to it. The excess of alkali remains free. Again, supposing an equivalent quantity of the terhydrate of phosphoric acid in solution, and one equivalent of soda added to it, one equivalent only of water is displaced, and two retained, and a phosphate formed, containing one of soda and two of water as bases, which is the salt already adverted to under its old name of biphosphate of soda. Let a second equivalent of soda be added to this salt, and a second basic atom of water is displaced, and a tribasic salt produced, containing two of soda and one of water as bases, which is the common phosphate of soda of pharmacy. A third equivalent of soda added to the last salt displaces the remaining atom of basic water, and a tribasic phosphate is formed, of which the whole three atoms of base are soda, and which has had the name of subphosphate of soda. But this last salt can unite with no more soda. The same three salts may be formed by means of the tribasic phosphate of water, in another manner. That acid hydrate decomposes chloride of sodium, but only to a certain extent, expelling hydrochloric acid, so as to acquire one of soda, and becoming 2HO , $\text{NaO} + \text{PO}_5$, or the biphosphate of soda (applying the old trivial terms); the same acid hydrate applied to the carbonate or the acetate of soda, can assume two proportions of soda, displacing twice as much of the weaker carbonic and acetic acids, as of the hydrochloric acid, and so becomes HO , $2\text{NaO} + \text{PO}_5$, or the common phosphate of soda; and the same acid hydrate applied to the hydrate of soda (caustic soda), assumes three of soda, and becomes $3\text{NaO} + \text{PO}_5$, or the subphosphate of soda.

From soluble tribasic phosphates, such as those mentioned, insoluble salts may be precipitated, which are likewise tribasic, by adding solutions of most metallic salts. Thus 1 equivalent of the common phosphate of soda, added to the nitrate of silver in excess, decomposes 3 equivalents of it, and produces the yellow tribasic phosphate of silver, as explained in the following diagram, in which the name of a substance is understood to express one equivalent of it, and the figures, numbers of equivalents:—



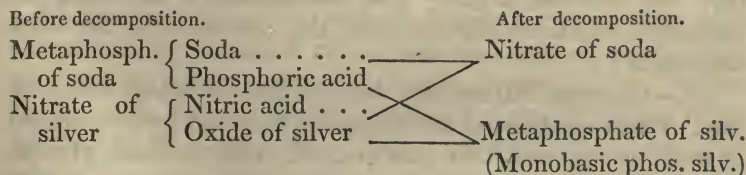
Here, then, is exact mutual decomposition, but it is attended with a phenomenon which does not occur when other neutral salts decompose each other. The liquid does not remain neutral, but becomes highly acid after precipitation; the reason is, that one of the new products is the nitrate of water, or hydrated nitric acid; and consequently the products, although neutral in composition, are not neutral to test paper.

The pyrophosphate of soda, which is bibasic, decomposes, on the other hand, two proportions of nitrate of silver, and gives a pyrophosphate or bibasic phosphate of silver, which is a white precipitate; thus—



Here there is no salt of water, among the products, and consequently the liquid is neutral after precipitation.

The metaphosphate of soda, which is monobasic, like the sulphates, nitrates and other familiar salts, decomposes, like them, but one proportion of nitrate of silver, and forms a white precipitate; thus—



If acetate or nitrate of lead be substituted for nitrate of silver in these decompositions, a tribasic, bibasic or monobasic salt of lead is obtained in the same manner; and these salts, again,

decomposed by sulphuretted hydrogen, afford respectively the terhydrate, deutohydrate and protohydrate of phosphoric acid. The statement of the decomposition of the metaphosphate of lead by sulphuretted hydrogen, will be sufficient to explain how a hydrate of phosphoric acid comes to be formed in all these cases :—

Before decomposition.		After decomposition.	
Metaphosph. of lead	{ Phosphoric acid	Metaphosph. of water (Protohydr. of phos. ac.)	
	{ Oxygen		
	{ Lead		
Sulphuretted hydrogen	{ Hydrogen . . .	Sulphuret of lead.	
	{ Sulphur		

It will be observed that the sulphuretted hydrogen forms an equivalent of water, at the same time that it throws down the sulphuret of lead; in this phosphate of lead, there is only one equivalent of oxide of lead, and consequently only one equivalent of water formed, but if there were two or three equivalents of oxide, there would be two or three equivalents of water formed; or the phosphoric acid is always left in combination with as many proportions of water as it previously possessed of oxide of lead. Thus the different hydrates of phosphoric acid are obtained, from the decomposition of the corresponding phosphates of lead.

In no decomposition of this kind, is there any transition from one class of phosphates into another, because the decompositions are always mutual, and the products of a neutral character. Hence an argument for retaining the trivial names, common phosphates, pyrophosphates and metaphosphates, for there is no changing, in decompositions by the humid way, from one to the other, and the salts comport themselves so far quite as if they had different acids. The circumstances may now be noticed, in which a transition from the one class to the other does occur :

1st.—Changes without the intervention of a high temperature. When solutions of the metaphosphate and pyrophosphate of water are warmed, they pass gradually into the state of common phosphate, combining with an additional quantity of water; and the metaphosphate of water appears then to become at once common phosphate, without passing through the intermediate state of hydration of the pyrophosphate. The

metaphosphate of barytes also, which is an insoluble salt, is gradually dissolved, when boiled in water, and becomes common phosphate. The easy transition from the one class of phosphates to the other, then witnessed, forbids the supposition that they contain different acids. It is remarkable that we may have pyrophosphates of potash and of ammonia in solution, and perfectly stable, but not in the dry state. These salts do not crystallize. The pyrophosphate of ammonia, indeed, when allowed to evaporate spontaneously, appears to crystallize, but in the act of becoming solid, it passes into common phosphate (the biphosphate of ammonia, $2\text{HO}, \text{NH}_4\text{O} + \text{PO}_5$), which is the salt that forms crystals.

2nd.—Changes with the intervention of a high temperature. If a single equivalent of phosphoric acid, anhydrous, or in any state of hydration, be calcined, at a temperature which may fall a little short of a red heat, (1°) with a single equivalent of soda or its carbonate, the metaphosphate of soda will be formed; (2°) with two equivalents of soda or its carbonate, the pyrophosphate of soda will be formed; and (3°) with three equivalents of soda or its carbonate, a common phosphate of soda will be formed. Hence, the formation of none of these classes is peculiarly the effect of a high temperature. Again, a tribasic phosphate, containing one or two equivalents of a volatile base, such as water or ammonia, loses the volatile base, when ignited, and the acid remains in combination with the fixed base. Hence, common phosphate of soda ($\text{HO}, 2\text{NaO} + \text{PO}_5$) is converted by heat into pyrophosphate ($2\text{NaO} + \text{PO}_5$), the original observation of Dr. Clark; and the biphosphate of soda ($2\text{HO}, \text{NaO} + \text{PO}_5$) into metaphosphate of soda ($\text{NaO} + \text{PO}_5$). The acid remains in combination with the fixed base left with it, and the salt produced may be dissolved in water without assuming basic water.

The metaphosphate of soda is susceptible of a remarkable conversion, by the agency of a certain temperature, and exhibits a change of nature, without a change of composition, such as often occurs in organic compounds, but rarely admits of so satisfactory an explanation. This particular salt, in common with all the other phosphates, combines with water, which becomes attached to the salt, in the state of constitutional water, or water of crystallization. The metaphosphate of soda, so hydrated, when dried at 212° , retains one equivalent of water,

but that water is not basic, for on dissolving the salt again, it is found still to be a metaphosphate. But let this hydrated metaphosphate be heated to 300° , and without losing anything, it changes completely, and becomes a pyrophosphate, the water which was constitutional before, being now basic. The formulæ of the salt in its two states, exhibits to the eye the nature of the internal change which has occurred in it:

- 1.—Hydrated metaphosphate of soda . $\text{NaO}, \text{PO}_5 + \text{HO}$,
- 2.—Pyrophosphate of soda and water . $\text{NaO}, \text{HO} + \text{PO}_5$.

In describing the three classes of phosphates, with their relations to each other, I have been thus minute, partly because considerable explanatory detail was required, from the extent of the subject, but principally that we might avail ourselves of the light which the phosphates have thrown upon the constitution of the class of organic acids, and upon the function of water in many compounds. Indeed, phosphoric acid is one of the links by which mineral and organic compounds are connected. And it may be reasonably supposed that it is that pliancy of constitution, which we have studied, that peculiarly adapts this, above all other mineral acids, to the wants of the animal economy.

SECTION X.

CHLORINE.

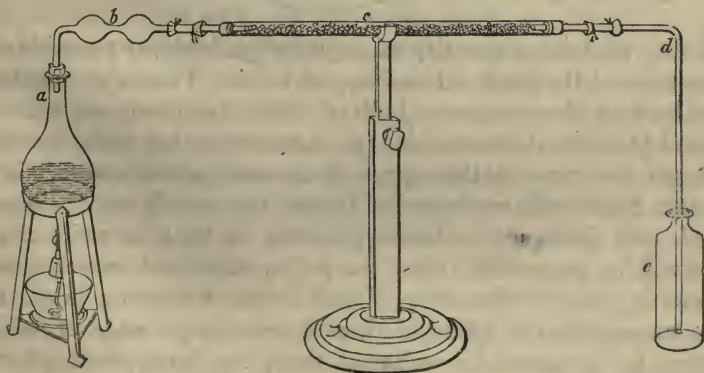
Eq. 442.65 or 35.47 ; Cl ; *density* 2440 ; .

This body was discovered by Scheele in 1774, but was believed to be of a compound nature, till Gay-Lussac and Thenard in 1809, shewed that it might reasonably be considered a simple substance. It is to the powerful advocacy of Davy, however, who entered upon the investigation shortly afterwards, that the establishment of the elementary character of chlorine is principally due, and to him it is indebted for the name it now bears, which is derived from *χλωρος*, yellowish green, and refers to its colour as a gas, elementary bodies being generally named from some remarkable quality or important circumstance in their history. Chlorine is the leading member of a well-marked natural family, to which also bromine, iodine and fluorine belong. Phosphorus, carbon, hydrogen, sulphur, and most of the pre-

ceding elementary bodies, have little or no action upon each other, or upon the mass of hydrogenous, carbonaceous and metallic bodies to which they are exposed in the material world; all these substances being too similar in nature, to have much affinity for each other. But the class to which chlorine belongs, ranks apart, and, with a mutual indifference to each other, they exhibit an intense affinity for the members of the other great and prevailing class, an affinity so general as to give the chlorine family the character of extraordinary chemical activity, and to preclude the possibility of any member of the class existing in a free and uncombined state in nature. The compounds again of the chlorine class, with the exception of those of fluorine, are remarkable for solubility, and consequently find a place among the saline constituents of sea water, and are of comparatively rare occurrence in the mineral kingdom; with the single exception of chloride of sodium, which besides being present in large quantity in sea water, forms extensive beds of rock salt in certain geological formations.

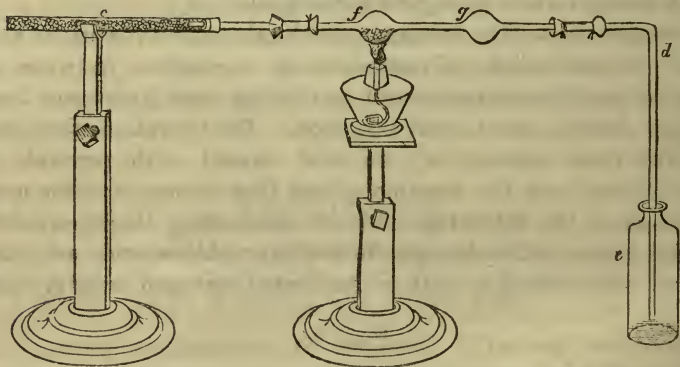
Preparation.—The fuming hydrochloric acid or muriatic acid (as it is also called) of commerce, is a solution in water of hydrochloric gas, a compound of chlorine and hydrogen, from which chlorine gas is easily procured. The liberation of chlorine results from contact of the acid named with peroxide of manganese, and the reaction which then occurs is made most obvious in the following mode of conducting the experiment. A few ounces of the strongly fuming hydrochloric acid, are introduced into a flask *a*, with a perforated cork and tube *b*, upon

FIG. 38.



which a bulb or two have been expanded; and that tube is connected by means of a short caoutchouc tube or *adopter*, with the tube *c*, containing fragments of chloride of calcium, and the last is connected in a similar manner with the exit tube *d*, which descends to the bottom of a dry and empty bottle *e*. Upon applying the spirit lamp, burning with a small flame to *a*, the liquid in the flask soon begins to boil, and the hydrochloric gas passes off, depositing perhaps a little moisture in the bulbs of *b*, which may be kept cool by wet blotting paper, and being completely dried in passing through *c*. It is conveyed by *d*, to the bottom of the bottle *e*, and finally escapes and produces white fumes in the atmosphere, after displacing the air of that bottle. The hydrochloric gas is obtained in *e* unchanged, and will redden and not bleach a little blue infusion of litmus poured into *e*. But between the tube *c* and *d*, let another tube be now interposed having a pair of bulbs blown upon it *f* and *g*, (Fig. 39) one of

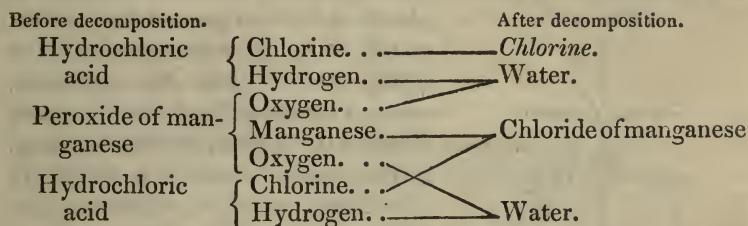
Fig. 39.



which *f* contains a quantity of pounded anhydrous peroxide of manganese; the bottle *e* remaining as before. Then upon applying heat to the manganese bulb *f*, the hydrochloric gas will be found to suffer decomposition as it traverses that bulb, its hydrogen uniting with the oxygen of the manganese and forming water, which will condense in drops in *g*, which may be kept cool, and disengaged chlorine proceeds on to *e*, in which that gas will be perceptible from its yellow tint, and more so by bleaching the infusion of reddened litmus remaining in *e*. If the transmission of hydrochloric acid over the peroxide of manganese be continued for sufficient time, the latter loses all its

oxygen, and the metal remains in the state of protochloride. Indeed only one half of the chlorine of the decomposed hydrochloric gas, is obtained as gas, the other half being retained by the manganese, as will appear by the following diagram :

Process for chlorine from hydrochloric acid and peroxide of manganese.

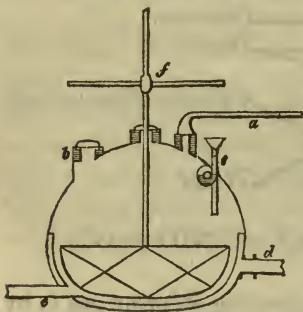


Or in symbols ; $\text{MnO}_2 + 2\text{HCl} = \text{MnCl}$ and 2HO and Cl .

The most convenient method of preparing chlorine gas is by mixing in a flask 2 ounces of peroxide of manganese, with 6 ounce measures of hydrochloric acid, diluted with an ounce or two of water to prevent it fuming. Effervescence, from escape of gas, takes place in the cold, but is greatly promoted by the application of a gentle heat. This gas is collected over water, of which the temperature should not be less than 90° , otherwise a great waste of the gas occurs from its solution in the water, and also a consequent annoyance to the operator from the escape of the chlorine into the atmosphere, by evaporation from the surface of the water trough. If the gas is not to be used immediately, but preserved, it should be collected in bottles, into which when filled with the gas, their stoppers greased, should be inserted before they are removed from the trough. Before the gas obtained by this process can be considered as pure, it should always be transmitted through water, to remove hydrochloric acid; an intermediate Wolfe's bottle containing water may be employed to wash the gas, as was done with sulphurous acid. If the gas is to be dried, it must be sent through a tube containing chloride of calcium, of two or three feet in length, great difficulty being experienced in drying this gas in a perfect manner, owing to its low diffusive power : it is three times more difficult to dry than carbonic acid. Chlorine cannot be collected over mercury, as it combines at once with that metal.

A somewhat different process for the preparation of chlorine is generally followed on the large scale. About 6 parts of manganese with 8 of common salt are introduced into a large leaden vessel, of a form nearly globular, as represented in the figure, and 5 or 6 feet in diameter, and to these are added as much of the unconcentrated sulphuric acid of the leaden chambers, as is equivalent to 13 parts of oil of vitriol. The leaden vessel is

FIG. 40.

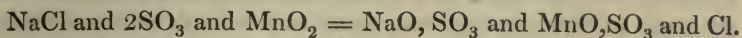


placed in an iron pan, or has a outer casing *d e*, as represented in the figure, and to heat the materials, steam is admitted by *d* into the space between the bottom and outer casing. In the figure, which is a section of the leaden retort, *a* represents the tube by which the chlorine escapes, *b* a large opening for introducing the solid material covered by a lid, or water valve, from the edges dipping into a channel containing water, *c* a twisted leaden funnel for introducing the acid, *f* a wooden agitator, and *e* a discharge tube, by which the waste materials are run off after the process is finished. A retort of lead cannot be used with safety, with peroxide of manganese and hydrochloric acid for chlorine, owing to the action of the acid upon the lead, and the evolution of hydrogen gas, which produces a spontaneously explosive mixture with chlorine. A material for the vessel, which might be substituted for glass, is still a desideratum in that process. Vessels of silver are acted upon, the chloride of silver appearing not to be absolutely insoluble in hydrochloric acid. In the reaction which occurs in the leaden retort, it may be supposed, either that hydrochloric acid is first liberated from chloride of sodium by sulphuric acid, and afterwards decomposed by peroxide of manganese, as in the preceding experiment; or that sulphates of manganese and soda are simultaneously formed, and chlorine liberated in consequence, as stated in the following diagram, in which the names express (as usual) single equivalents :

Process for chlorine from chloride of sodium (common salt), peroxide of manganese and sulphuric acid :

Before decomposition.		After decomposition.
Chloride of sodium	{ Chlorine. Sodium.	Chlorine.
Sulphuric acid..	Sulphuric acid. .	Sulphate of soda
Peroxide of manganese	{ Oxygen. Protox. manga.	
Sulphuric acid..	Sulphuric acid. .	Sulp. of manga.

Or in symbols ;



Properties.—Chlorine is a dense gas of a pale yellow colour, having a peculiar suffocating odour, absolutely intolerable even when largely diluted with air, and occasioning great irritation in the trachea, with coughing, and oppression of the chest. Some relief from these effects is experienced from the inhalation of the vapour of ether or alcohol. The density of chlorine gas is, by experiment 2470, by theory 2440. Under a pressure of about 4 atmospheres, chlorine condenses into a limpid liquid of a bright yellow colour, of a sp. gr. about 1.33, and which has not been frozen. Water at 60° dissolves twice its volume of this gas, and acquires the yellowish colour, odour and other properties of chlorine. To form chlorine water, a stout bottle filled with the gas at the tepid water trough, may be closed with a good cork and removed to a bason of cold water; on loosening the cork with the head of the bottle under water, a little water will enter it, from the contraction of the gas by cooling; and this water may be agitated in contact with the gas, by a lateral movement of the bottle, without removing it from the water; on loosening the cork again more water will be found to enter the bottle, and by repeating the agitation and admission of water, the whole gas (if pure) is absorbed, and the bottle is in the end filled with water, which of course contains an equal volume of chlorine gas. With water near its freezing point, chlorine combines and forms a crystalline hydrate, which Faraday found to contain 10 atoms of water. Hence, chlorine gas cannot be collected at all over water, below 40°. Exposed to light, chlorine water soon loses its properties, water being decomposed and hydrochloric acid formed, with the evolution of oxygen gas. But it may be preserved for a long time in a stone-ware bottle. When diluted so far that the water does not con-

tain above 1 or $1\frac{1}{2}$ per cent of its bulk of chlorine, the odour is by no means strong, and such a solution may be employed in bleaching, without inconvenience to the workmen, although a combination of chlorine with hydrate of lime, called the chloride of lime, is generally preferred for that purpose.

Chlorine does not in any circumstances unite directly with oxygen, although several compounds of these elements can be formed; nor does it combine directly with nitrogen or carbon. Chlorine and hydrogen gases may be mixed and preserved in the dark without uniting, but combination is determined with explosion by spongy platinum or the electric spark, or by exposure to the direct rays of the sun; even under the diffuse light of day, combination of the gases takes place rapidly, but without explosion. Chlorine indeed has a strong affinity for hydrogen, and decomposes most bodies containing that element, hydrochloric acid being always formed. In plunging an ignited taper into chlorine gas, its flame is extinguished, but the column of oily vapour rising from the wick is rekindled by the chlorine, and the hydrogenous part of the combustible continues to burn with a red and smoky flame, which expires on removing the taper into air. Paper dipt in oil of turpentine takes fire spontaneously in this gas, and the oil burns with the deposition of a large quantity of carbon. The affinity of chlorine for most metals is equally great: antimony, arsenic and several others, showered in powder into this gas, take fire and produce a brilliant combustion. Chlorine is absorbed by alcohol and many other organic substances, when it generally eliminates more or less hydrogen, as hydrochloric acid, and enters also by substitution into the original compound, in the place of that hydrogen, thus producing many new compounds, such as chloral from alcohol. It bleaches all vegetable and animal colouring matters, and is believed then to act in that manner. The colours are destroyed and cannot be revived by any treatment.

Chlorine when free is easily recognized by its odour and bleaching power, and in the soluble chlorides, by producing with nitrate of silver, a white curdy precipitate of chloride of silver, which is soluble in ammonia, but not soluble in cold or boiling nitric acid.

Uses.—Chemistry has presented to the arts few substances of which the applications are more valuable. Chlorine is the dis-

colouring agent of the modern process of bleaching, which as it is generally conducted with cotton goods, consists of the following operations. The cloth, after being well washed, is boiled first in lime-water and then in caustic soda, which remove from it certain resinous matters soluble in alkali. It is then steeped in a solution of chloride of lime, so dilute as just to taste distinctly, which has little or no perceptible effect in whitening it; but the cloth is afterwards thrown into water acidulated with sulphuric acid, of sp. gr. between 1.010 and 1.020, when a minute disengagement of chlorine takes place throughout the substance of the cloth, and it immediately assumes a bleached appearance. The cloth is boiled a second time with caustic soda, and digested again in dilute chloride of lime, and in dilute sulphuric acid as before. The acid favours the bleaching action, and is required besides to remove the caustic alkali, a portion of which adheres pertinaciously to the cloth. The fibre of the cloth is not injured by dilute sulphuric acid, although digested in it for days, provided the cloth is not allowed to dry with the acid in it, or left above the surface of the liquor. But it is very necessary to wash well after the last *souring*, to get rid of every trace of acid, with which view the cloth may be passed through warm water, as a precautionary measure to finish with.

When employed for the purpose of disinfecting the wards of hospitals, chlorine is most conveniently evolved from chloride of lime, of which a pound may be mixed with water in a hand-bason, and a pound measure of hydrochloric acid poured upon it. The gas is evolved from these materials without heat.

Chlorides.—Chlorine combines with all the metals and in the same proportions as oxygen. With the exception of the chlorides of silver and lead, and subchlorides of copper and mercury, these compounds are soluble and sapid, and they possess in an eminent degree the saline character. Indeed common salt, the chloride of sodium, has given its name to the class of salts, and chlorine is the type of salt-radicals or *halogenous* (salt-producing) bodies. Chlorides of metals belonging to different classes often combine together and form double chlorides; the chlorides of the potassium family, in particular, with some chlorides of the magnesian family, as with chloride of copper, with chloride of mercury, with both the chlorides of tin, and with perchlorides generally. A chloride and oxide of the same metal (excepting

the potassium family) often combine together, forming *oxichlorides*, which are in general of slight solubility.

Chlorine is also absorbed by alkaline solutions, and combinations are formed which bleach and exhibit many of the properties of the free element. The state of the chlorine in these compounds and also in dry chloride of lime, formed by exposing hydrate of lime to chlorine gas, is still matter of uncertainty. But they are not permanent compounds, and the chlorine eventually acts upon the metallic oxide, so as to produce a chloride, a chlorate of the metal as will be afterwards explained.

The following chlorides of the non-metallic elements will now be particularly described :

Hydrochloric acid. . . H Cl	Subchloride of carbon. $C_4 Cl_2$
Hypochlorous acid. . . Cl O	Chlorocarbonic acid. . $CO_2 Cl$
Peroxide of chlorine. . $Cl O_4$	Chloride of boron. . B Cl_3
Chloric acid. . . Cl O_5	Chloride of silicon. . Si Cl_3
Hyperchloric acid. . Cl O_7	Chloride of sulphur. . $S_2 Cl$
Chloride of nitrogen. . N Cl_3	Bichloride of sulphur. S Cl_2
Perchloride of carbon. . $C_4 Cl_6$	Terchl. of phosphorus. P Cl_3
Protochloride of carbon. $C_4 Cl_4$	Perchl. of phosphorus. P Cl_5

HYDROCHLORIC ACID.

Syn. CHLORHYDRIC ACID (*Thenard*), MURIATIC ACID. *Eq.*
455.13 or 36.47 ; ClH ; density 1269.5 ;

.

This acid is one of the most frequently employed reagents in chemical operations, and has long been known under the names of spirit of salt, marine acid, and muriatic acid (from *murias*, sea-salt). It was first obtained by Priestley in its pure form of a gas, in 1772.

Preparation.—Hydrochloric acid is always obtained by the action of oil of vitriol upon common salt. When the process is conducted on a small scale and in a glass retort, equal weights of common salt, oil of vitriol and water may be taken. The oil of vitriol being mixed with 1-3rd of the water in a thin flask, and cooled, is poured upon the salt contained in a capacious retort. A clean flask containing the remaining 2-3rds of the water is then adapted to the retort as a condenser, as in the distillatory apparatus figured at page 59. Upon applying heat to

the retort, hydrochloric acid gas comes off and is condensed in the receiver, affording an aqueous solution of the acid, of sp. gr. 1.170, and which contains about 37 per cent of dry acid; while a mixture of sulphate and bisulphate of soda remains in the retort. Supposing single equivalents of oil of vitriol and chloride of sodium to be employed, to which the preceding proportions approximate, then the rationale of the action is as follows:

Process for hydrochloric acid:

Before decomposition.		After decomposition.	
733 Chloride of sodium	{ Chlorine. . 442 { Sodium. . 291 Hydrogen. . 12½	454½ hydroc. acid	
613½ Oil of vitr.	{ Oxygen. . . 100 { Sulphu. acid 501		892 sulph. of soda
1346½	1346½	1346½	

Or in symbols; NaCl and $\text{HO},\text{SO}_3 = \text{HCl}$ and NaO,SO_3 .

This process is more economically conducted on the large scale in a cast iron cylinder, about 5 feet in length and 2½ in diameter, laid upon its side, which has moveable ends, generally composed of a thin paving stone cut into a circular disc and divided into two unequal segments. A charge of three or four cwt. of salt is introduced into the retort, and after the bottom is heated, undiluted oil of vitriol is added in a gradual manner by means of a long funnel, and in proportion not exceeding the equivalent for the chloride of sodium. In such circumstances, the lower part of the cylinder exposed to the sulphuric acid is not much acted upon, while the roof of the cylinder is protected from the hydrochloric acid fumes by a coating of fire-clay or thin split bricks. The hydrochloric acid gas is conducted by a strong glass tube into a series of large jars of salt-glaze ware, connected with each other like Wolfe's bottles, and containing water in which the acid condenses.

Properties.—Hydrochloric acid is obtained in the state of gas by boiling an ounce or two of the fuming aqueous solution, in a small retort, or by pouring oil of vitriol upon a small quantity of salt in a retort, and is collected over mercury. It is an invisible gas, of a pungent acid odour, and produces white fumes

when allowed to escape, by condensing the moisture in the air. By a pressure of 40 atmospheres at 50° it is condensed into a liquid, of sp. gr. 1.27. It is quite irrespirable but much less irritating than chlorine; it is not decomposed by heat alone, nor when heated in contact with charcoal. Hydrochloric acid extinguishes combustion, and is not made to unite with oxygen by heat; but when electric sparks are passed through a mixture of this gas and oxygen, decomposition takes place to a small extent, water being formed and chlorine liberated. It is composed by volume, of one combining measure or 2 volumes of each of its constituents, united without condensation; so that its combining measure is 4 volumes, and its theoretical density 1269.5. It may be formed directly by the union of its elements.

If a few drops of water or a fragment of ice be thrown up into a jar of hydrochloric acid over mercury, the gas is completely absorbed in a few seconds; or if a stout bottle filled with this gas be closed with the thumb and opened under water, an instantaneous condensation of the gas takes place, water rushing into the bottle as into a vacuum. Dr. Thomson finds that 1 cubic inch of water absorbs 418 cubic inches of gas, at 69°, and becomes 1.34 cubic inch. He has constructed the following table, from experiment, of the specific gravity of hydrochloric acid of determinate strengths.*

HYDROCHLORIC ACID.

Atoms of Water to 1 of Acid.	Real Acid in 100 of the liquid.	Specific Gravity.	Atoms of Water to 1 of Acid.	Real Acid in 100 of the liquid.	Specific Gravity.
6	40.66	1.203	14	22.700	1.1060
7	37.00	1.179	15	21.512	1.1008
8	33.95	1.162	16	20.442	1.0960
9	31.35	1.149	17	19.474	1.0902
10	29.13	1.139	18	18.590	1.0860
11	27.21	1.1285	19	17.790	1.0820
12	25.52	1.1197	20	17.051	1.0780
13	24.03	1.1127			

To this may be added the following useful table, for which we are indebted to Mr. E. Davy:—

* First Principles of Chemistry.

HYDROCHLORIC ACID.

Specific Gravity.	Quantity of Acid per cent.	Specific Gravity.	Quantity of Acid per cent.
1.21	42.43	1.10	20.20
1.20	40.80	1.09	18.18
1.19	38.38	1.08	16.16
1.18	36.36	1.07	14.14
1.17	34.34	1.06	12.12
1.16	32.32	1.05	10.10
1.15	30.30	1.04	8.08
1.14	28.28	1.03	6.00
1.13	26.26	1.02	4.04
1.12	24.24	1.01	2.02
1.11	22.22		

It thus appears that the strongest hydrochloric acid that can be easily formed contains six atoms of water ; this liquid allows acid to escape when evaporated in air, and comes according to an observation of my own, to contain 12 atoms of water to 1 of acid. Distilled in a retort, it was found, by Dr. Dalton, to lose more acid than water till it attained the specific gravity 1.094, when its boiling point attained a maximum 230°, and the acid then distilled over unchanged. Dr. Clark finds by careful experiments that the acid which is unalterable by distillation, contains 16.4 equivalents of water.

The concentrated acid is a colourless liquid, fuming strongly in air, highly acid, but less corrosive than sulphuric acid ; not poisonous when diluted. It is decomposed by substances which yield oxygen readily, such as metallic peroxides and nitric acid, which cause an evolution of chlorine, by oxidating the hydrogen of the hydrochloric acid. A mixture of 1 measure of nitric and 2 measures of muriatic acid forms *aqua regia*, which dissolves the less oxidable metals, such as gold and platinum, through the agency of the disengaged chlorine.

The hydrochloric acid of commerce has a yellow or straw colour, which is generally due to a little iron, but may be occasionally produced by organic matter, as it is sometimes destroyed by light. This acid is rarely free from sulphuric acid, the presence of which is detected by the appearance of a white precipitate of sulphate of barytes, on the addition of chloride of barium to the hydrochloric acid diluted with 4 or 5 times its bulk of distilled water. Sulphurous acid is also occasionally present in commercial hydrochloric acid, and is indicated by the addition of a few crystals of protochloride of tin, which salt

decomposes sulphurous acid and occasions, after standing some time, a brown precipitate containing sulphur in combination with tin (Girardin.) To purify hydrochloric acid, it should be diluted till its sp. gr. is about 1.1, for which the strongest acid requires an equal volume of water; and with the addition of a portion of chloride of barium, the acid should then be redistilled. As the acid brings over enough of water to condense it, Liebig's condensing apparatus (page 60) can be used in this distillation. The pure acid thus obtained is strong enough for almost every purpose, and has the advantage of not fuming in the air. Hydrochloric acid, like chlorine and the soluble chlorides, gives with nitrate of silver a white curdy precipitate, the chloride of silver, soluble in ammonia, but not dissolved by hot or cold nitric acid.

Hydrochloric acid belongs to the class of hydrogen acids, or hydracids, which do not exist in salts. On neutralizing this acid with soda or any other basic oxide, no hydrochlorate of soda is formed, but the hydrogen of the acid with the oxygen of the soda forming water, the chlorine and sodium combine and produce a metallic chloride. Zinc and the other metals which dissolve in dilute sulphuric acid, with evolution of hydrogen, dissolve with equal facility in this acid, with the same evolution of hydrogen, and a chloride of the metal is formed.

COMPOUNDS OF CHLORINE AND OXYGEN.

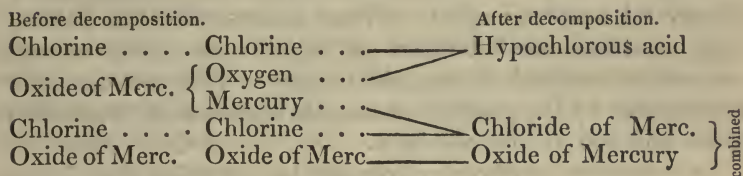
Chlorine and oxygen gases exhibit no disposition to combine with each other in any circumstances, but this is not inconsistent with their forming a series of compounds, as nitrogen and oxygen, which exhibit a similar indifference to each other also do. The oxides of chlorine are four in number, and all bear acid appellations, namely:

Hypochlorous acid.	.	.	.	Cl O
Chlorous acid.	.	.	.	Cl O ₂
Chloric acid.	.	.	.	Cl O ₃
Hyperchloric acid.	.	.	.	Cl O ₄

Hypochlorous and chloric acids are always primarily formed by a reaction occurring between chlorine and two different classes of metallic oxides; and the chlorous and hyperchloric acids again are derived from the decomposition of chloric acid.

Hypochlorous acid.—The discovery of this compound was made by M. Balard in 1834.* It is formed by the action of chlorine upon the red oxide of mercury. If to a two-pound bottle of chlorine gas, 6 drachms of red oxide of mercury in fine powder be added, with $1\frac{1}{2}$ ounce of water, the chlorine will be found to be rapidly absorbed on agitation. One portion of the chlorine unites with the oxygen of the metallic oxide, and becomes hypochlorous acid, which is dissolved by the water, while another portion forms a chloride with the metal, which chloride unites with a portion of undecomposed oxide, and forms an insoluble oxichloride. The liquid may be poured off and allowed to settle ; it is a solution of hypochlorous acid, with generally a little chloride of mercury. This reaction is expressed in the following diagram :—

FORMATION OF HYPOCHLOROUS ACID.



Or in symbols ; 2 Cl and $2 \text{ HgO} = \text{ClO}$ and HgCl , HgO . But the oxichloride formed, seems not always to contain the same proportion of oxide. The proportion of hypochlorous acid in the liquid may be increased, by introducing the same solution into a second bottle of chlorine, with an additional quantity of red oxide of mercury. The oxide of zinc and black oxide of copper, diffused through water, and exposed to chlorine, give rise to a similar formation of hypochlorous acid.

The pure hypochlorous acid is a gas, which Balard succeeded in disengaging by passing up fragments of nitrate of lime into the liquid acid above mercury, in a jar of the mercurial trough. By dissolving in the water, that salt causes the evolution of the gas, which collects in the upper part of the jar, and is defended from contact with the mercury, which absorbs it, by the intervention of the saline solution.

* An. de Ch. et de Ph. t. 57, p. 225, or Taylor's Scientific Memoirs, vol. I, p. 269.

The gas is of a pale yellow colour, very similar to chlorine. It is composed of 2 volumes of chlorine and 1 volume of oxygen, condensed into 2 volumes, and is resolved by a slight elevation of temperature into its constituent gases. This decomposition is attended with an explosion of such violence as to project the jar from the trough, but not to break it to pieces, and may occur on transferring the gas from one jar into another. Water dissolves about 100 volumes of this gas.

The original solution of hypochlorous acid may be distilled, but much of the acid is decomposed unless the operation be conducted in vacuo. It is then obtained as a transparent liquid of a slightly yellow colour. It displaces the carbonic acid of alkaline carbonates, but has not much analogy to other acids. Its taste is extremely strong and acrid, but not sour, and its odour penetrating and different from, although somewhat similar to chlorine. It attacks the epidermis like nitric acid, and is exceedingly corrosive. It bleaches instantly, like chlorine, and is a powerful oxidizing agent. When concentrated it is exceedingly unstable, small bubbles of chlorine gas being spontaneously evolved and chloric acid formed. This decomposition is promoted by the presence of angular bodies, such as pounded glass, and also by heat and light.

Of the elementary bodies, hydrogen has no action upon hypochlorous acid. Sulphur, selenium, phosphorus and arsenic act upon it with great energy, and are all of them raised to their highest degree of oxidation, with the evolution of chlorine gas; selenium even being converted into selenic acid, although it is only converted into selenious acid by the action of nitric acid. Iodine is also converted into iodic acid. Iron filings decompose it immediately and chlorine comes off. Copper and mercury combine with both elements of the acid and form oxichlorides. Many other metals are not acted upon by it, unless another acid be present, such as zinc, tin, antimony and lead. Silver has a different action upon hypochlorous acid from that of most bodies, combining with its chlorine and causing an evolution of oxygen gas. Hydrochloric and hypochlorous acids mutually decompose each other, water being formed, and chlorine liberated; the presence of soluble chlorides is equally incompatible with the existence of hypochlorous acid.

Hypochlorites.—The direct combination of hypochlorous acid with powerful bases is accompanied by heat, which is apt

to convert the hypochlorite into a mixture of chlorate and chloride; but by adding the acid in a gradual manner to the alkaline solution, hypochlorites of potash, soda, lime, barytes and strontian may be formed, and may even be obtained in a solid state by evaporation in vacuo, if a considerable excess of alkali be present, which appears to give a certain degree of stability to these salts. They bleach powerfully, and their odour and colour are identically the same as the corresponding decolorizing compounds of chlorine, from which it is impossible to distinguish them by their physical properties. They are salts of a very changeable constitution; a slight increase of temperature, the influence of solar light, even of diffused light, converts them into chlorides and chlorates. It is the opinion of M. Balard that bleaching powder, formed by exposing hydrate of lime to chlorine, is a mixture of hypochlorite of lime and chloride of calcium; but to this subject I shall again return under the salts of lime.

The *euchlorine* gas of Davy, to which he assigned the composition of hypochlorous acid, has been found to be a mixture of chlorine and chlorous acid gases. That mixture is obtained by the action of hydrochloric acid of sp. gr. 1.1 upon chlorate of potash, aided by a gentle heat. It has a very yellow colour (*euchlorine*), and explodes feebly when a hot wire is introduced into it, becoming nearly colourless, when the chlorous acid is decomposed.

Chloric acid, ClO_5 .—When a stream of chlorine gas is transmitted through a strong solution of caustic potash, the gas is absorbed, and a solution is formed which bleaches at first, but loses that property without any escape of gas, and becomes a mixture of chloride of potassium and chlorate of potash, the latter of which, being the least soluble, separates in shining tabular crystals. Five equivalents of potash (the oxide of potassium) are decomposed by 6 of chlorine, 5 of which unite with the potassium and form 5 equivalents of chloride of potassium, while the 5 of oxygen form chloric acid with the remaining equivalent of chlorine, as stated in the following diagram:—

ACTION OF CHLORINE UPON POTASH.

Before decomposition.		After decomposition.	
5 Chlorine .	5 Chlorine .	5 Chloride of potassium.	
5 Potash .	{ 5 Potassium		
	{ 5 Oxygen .	Chloric acid } Chlorate of	
Chlorine . .	Chlorine .		
Potash . . .	Potash . . .	Potash	} potash.

Or in symbols : 6Cl and $6\text{KO} = \text{KO}, \text{ClO}_5$ and 5KCl . Such is the nature of the action of chlorine upon the soluble and highly alkaline metallic oxides.

The chlorate of barytes may be formed by transmitting chlorine through caustic barytes in the same manner; and from a solution of the pure chlorate of barytes, chloric acid may be obtained by the cautious addition of sulphuric acid, so long as it occasions a precipitate of sulphate of barytes. The solution may be evaporated by a very gentle heat till it becomes a syrupy liquid, which has no odour, but a very acid taste, is decomposed above 100° , and when distilled at a still higher temperature gives water, then a mixture of chlorine and oxygen gases, and hyperchloric acid, which may be prepared in this way without difficulty. Chloric like nitric acid, is not isolable, being incapable of existing, except in combination with water or a fixed base. This acid first reddens litmus paper, but after a time the colour is bleached, and if the acid has been highly concentrated, the paper often takes fire. It dissolves zinc and iron with disengagement of hydrogen. Chloric acid is decomposed by hydrochloric acid, with escape of chlorine, and by most combustible bodies and acids of the lower degrees of oxidation, such as sulphurous and phosphorous acids, which oxidate themselves at its expense.

This acid when free, or in combination, may be recognized by several properties. It is not precipitated by chloride of barium or nitrate of silver, and has no bleaching power; sulphuric acid causes the disengagement from it of a yellow gas, having a peculiar odour, which bleaches strongly; and its salts when heated to redness afford oxygen, and deflagrate with combustibles.

Chlorates.—This class of salts is remarkable for a general solubility, like the nitrates. Those of them which are fusible detonate with extreme violence with combustibles. The chlorate of potash, of which the preparation and properties will be described under the salts of potash, has become a familiar chemical product, being largely consumed in the manufacture of deflagrating mixtures. The chlorates were at one time termed *hyperoxymuriates*, and their acid, the existence of which was originally observed by Mr. Chenevix, was first obtained in a separate state by Gay-Lussac.

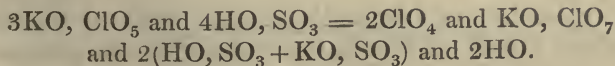
Hyperchloric acid, ClO_7 .—This acid, which is also called

perchloric and oxichloric acid, is obtained from chlorate of potash in different ways. At that particular point of the decomposition of chlorate of potash by heat, when the evolution of oxygen is about to become very violent, the fused salt is in a pasty state, and contains, as was first observed by Serullas, a considerable quantity of hyperchlorate, the oxygen extricated from one portion of chlorate being retained by another portion of the same salt. This salt is rubbed to powder, and dissolved in boiling water, from which the hyperchlorate is first deposited, on cooling, owing to its sparing solubility. The same salt may also be prepared by throwing chlorate of potash in fine powder and well dried, into oil of vitriol gently heated in an open bason, by a few grains at a time, when the liberated chloric acid resolves itself into chlorous acid and hyperchloric acid, the former coming off as a yellow gas; thus :—

RESOLUTION OF CHLORIC ACID INTO CHLOROUS ACID AND
HYPERCHLORIC ACID.

Before decomposition.		After decomposition.
3 Chloric acid	2 Chlorine	2 Chlorous acid.
	8 Oxygen	
	7 Oxygen	
	Chlorine	Hyperchloric acid.

Of the 3 equivalents of potash, previously in combination with the chloric acid, one remains with hyperchloric acid as hyperchlorate of potash, and the other two are converted into bisulphate of potash. The whole reaction between the acid and salt may, therefore, be thus expressed :—



In conducting this operation, the greatest caution is necessary, owing to the explosive property of chlorous acid; for if the order of mixing the substances be reversed, and the acid poured upon the chlorate, or if too much chlorate be added at a time to the acid, a most violent and dangerous detonation may occur. But this reaction is chiefly interesting as affording chlorous acid; for hyperchlorate of potash may be obtained from chlorate by the action of nitric acid, lately observed by Professor Penny, without danger or inconvenience. The chlorate is tranquilly decomposed in nitric acid gently heated upon it, the chlo-

rine and oxygen of 3 equivalents of chlorous acid being evolved in a state of mixture and not of combination ; the saline residue consists of 3 equivalents of nitrate and 1 of hyperchlorate of potash, which may be separated by dissolving them in the smallest adequate quantity of boiling water. On cooling, the hyperchlorate separates in small shining crystals, which may be dissolved a second time to obtain them perfectly pure.

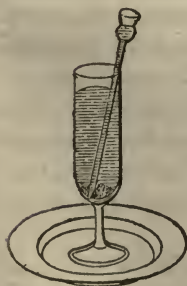
Hyperchloric acid may be prepared from this salt by boiling it with an excess of fluosilicic acid, which forms, with potash, a salt nearly insoluble. After cooling, the clear liquid is decanted and evaporated by a water bath. To eliminate a small excess of hydrofluoric acid, a little silica in fine powder is added to the liquid, which at a certain degree of concentration carries off the former as fluosilicic acid. After being still further concentrated, the acid liquid may be distilled in a retort by a sandbath heat. A very dilute acid comes over first, but the temperature of ebullition rises till it attains 392° , after which the receiver should be changed, because what then passes over is a concentrated acid of sp. gr. 1.65. This acid is a colourless liquid which fumes slightly in the air. It may be still farther concentrated by distilling it with 4 or 5 times its weight of strong sulphuric acid, when the greater part of it is decomposed into chlorine and oxygen, but a portion condenses in a mass of small crystals, and also in long four-sided prismatic needles terminated by dihedral summits, which according to Serullas are two different hydrates of the acid, the last containing least water and being most volatile. The crystals and the concentrated solution of the acid have a great affinity for water ; the acid itself appears not to be isolable.

The hyperchloric acid is much the most stable of the oxides of chlorine ; it does not bleach, is not altered by the presence of sulphuric acid, and is not decomposed by sulphurous acid or by sulphuretted hydrogen. It dissolves zinc and iron with effervescence, and in point of affinity, is one of the most powerful acids. Hyperchloric acid is recognized by producing, with potash, a salt of the same sparing solubility as bitartrate of potash. It is an interesting acid from its composition, and as being the most accessible of the small class containing hyperiodic and hypermanganic acids, to which it belongs. The alkaline hyperchlorates emit much oxygen, when heated, and leave metallic chlorides ; they do not deflagrate so powerfully with combustibles as the chlorates.

Chlorous acid or peroxide of chlorine, Cl O_4 .—This acid cannot be obtained in a state of purity, without considerable danger. Gay-Lussac recommends, in preparing it, to mix chlorate of potash into the state of a paste with sulphuric acid previously diluted with half its weight of water and cooled, and to distil the mixture in a small retort by a water-bath. It comes off as a gas, of a yellow colour considerably deeper than chlorine, which must be collected over mercury. It is composed of 2 volumes of chlorine with 4 volumes of oxygen, condensed into 4 volumes, which gives it a density of 2337.5. This gas is decomposed gradually by light, but between 200° and 212° its elements separate in an instantaneous manner, with the disengagement of light and a violent explosion which breaks the vessels. Water dissolves 7 volumes of this gas, and the gas itself may be liquefied by pressure. It bleaches damp litmus paper, without first reddening it, and is absorbed by alkaline solutions with the formation according to Martens of a peculiar class of decolorizing salts.* These, however, readily pass into chlorates and chlorides, like the hypochlorites of Balard, when their solutions are heated.

Chlorous acid has a violent action upon combustibles, kindling phosphorus, sulphur, sugar and other combustible substances in contact with which it is evolved. Its action upon phosphorus

FIG. 41.



may be shewn by throwing a drachm or two of crystallized chlorate of potash into a deep foot-glass or ale-glass (see figure 41) filled with cold water, to the bottom of which the salt falls without much loss by solution. Oil of vitriol is then conducted to the salt, in a small stream, from a tube funnel, the lower end of which has been drawn out into a jet with a minute opening. A gas of a lively yellow colour is evolved with slight concussions, and immediately dissolved by the water, to which it imparts the same colour. If while this is occurring a piece of phosphorus be thrown into the glass, it

is ignited by every bubble of gas, and a brilliant combustion is produced under the water, forming a beautiful experiment wholly without danger. If a few grains of chlorate of potash in

* An. de Ch. et de Ph. t. 61, p. 293.

fine powder and loaf-sugar, be mixed upon paper by the fingers, (rubbing these substances together in a mortar may be attended with a dangerous explosion,) and a single drop of sulphuric acid be allowed to fall from a glass rod upon the mixture, an instantaneous deflagration takes place, occasioned by the evolution of the yellow gas which ignites the mixture. Captain Manby used to fire in this manner the small piece of ordnance, which he proposed as a life-preserver, to throw a rope over a stranded vessel from the shore; and the same mixture was afterwards employed, with sulphuric acid, in various forms of the instantaneous light match, all of which, however, are now superseded by other mixtures ignited by friction without sulphuric acid.

OTHER COMPOUNDS OF CHLORINE.

Chloride of nitrogen, N Cl_3 .—This is one of the most formidable of explosive compounds, and great caution is necessary in its preparation, to avoid accidents. Four ounces of sal ammoniac, which must not smell of animal matter, are dissolved in a small quantity of boiling water, filtered, and made up to 3 pounds with distilled water; a two pound bottle of chlorine is inverted in a bason containing this solution at 90° , being supported by the ring of a retort stand, with its mouth over a small leaden saucer. The chlorine gas is absorbed, and upon the surface of the liquid, which rises into the bottle, an oily substance condenses, which when it accumulates, precipitates in large drops, and is received in the leaden saucer. During the whole operation, the bottle must not be approached, unless the face is protected by a sheet of wire gauze, and the hands by thick woollen gloves; agitation of the bottle, to make the suspended drop fall, is a most common cause of explosion. The leaden saucer, when it contains the chloride, may be withdrawn from under the bottle, without disturbing the latter, and then no harm can result from the explosion, if it does not occur in contact with glass.

M. Balard finds that this compound may also be produced by suspending a mass of sulphate of ammonia in a strong solution of hypochlorous acid.

The chloride of nitrogen is a volatile oleaginous liquid of a deep yellow colour, and sp. gr. 1.653, of which the vapour is irritating like chlorine and attacks the eyes. It may be distilled at 160° , but effervesces strongly at 200° and explodes

between 205° and 212° , producing a very loud detonation, and shattering to pieces glass or cast-iron, but producing merely an indentation in a leaden cup. It is resolved into chlorine and nitrogen gases, the instantaneous production of which with heat and light, is the cause of the violence of the explosion. The chloride of nitrogen is decomposed by most organic matters containing hydrogen; and may be safely exploded by touching it with the point of a cane-rod, which has been previously dipt in oil of turpentine.

The properties of this compound render its accurate analysis almost impossible, and the correctness of the formula usually assigned to it is very doubtful. M. Millon has shewn that it may contain hydrogen, and is possibly a compound of chlorine with amidogen, NH_2Cl . He formed from it corresponding compounds, containing bromine, iodine and cyanogen, by double decomposition, a bromide, iodide or cyanide of potassium being introduced into the chloride of nitrogen for that purpose.*

CHLORIDES OF CARBON.

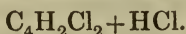
Perchloride of carbon, C_4Cl_6 .—The compounds of these elements are not formed directly, but were produced by Mr. Faraday by the action of chlorine upon a certain compound of carbon and hydrogen, and the circumstances of their formation have been explained lately with singular felicity by M. Regnault. Chlorine and olefiant gas C_4H_4 combine together in equal volumes, and condense as an oily looking body, of an ethereal odour, which is known as the Dutch liquid, from having been first formed by certain associated Dutch chemists, and also as the chloride of olefiant gas, although the latter term is objected to as incorrect in theory. Chemists have now agreed, after much discussion, that the formula of this liquid is not $\text{C}_4\text{H}_4 + 2\text{Cl}$, but that its elements are thus arranged:—

Dutch liquid. . . . $\text{C}_4\text{H}_3\text{Cl} + \text{HCl}$.

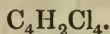
It is a combination of hydrochloric acid HCl , with the chloride of acetyl $\text{C}_4\text{H}_3\text{Cl}$. Acetyl, or as it is also called aldehydene (C_4H_3) pervades an extensive series of compounds, aldehydic and acetic acids, for instance, being oxides of this radical, namely $\text{C}_4\text{H}_3 + 2\text{O}$, and $\text{C}_4\text{H}_3 + 3\text{O}$; and these com-

* An. de Ch. et de Ph. t. 69, p. 75.

pounds may be traced up to alcohol, the substance from the decomposition of which, indeed, this whole class of compounds is primarily derived. Thus acetyl with two equivalents of hydrogen forms a higher compound radical ethyl C_4H_3, H_2 or C_4H_5 , of which ether is the oxide, and alcohol the hydrate of that oxide. In both the acetyl and ethyl series, it will be observed that the proportion of carbon (C_4) is constant, being that originally present in the alcohol, and we shall find it in the chloride of carbon, which is the last product of reducing processes upon alcohol. Olefiant gas itself is a hydruret of acetyl that is, C_4H_3, H . When exposed to chlorine, both the acetyl and hydrogen combine with chlorine, giving the Dutch liquor, $C_4H_3, Cl + HCl$. Comparing the formula for olefiant gas with the first part of the last formula, C_4H_3, H with C_4H_3, Cl , it will be found that in losing an atom of hydrogen the olefiant gas has acquired an atom of chlorine; and this is an instance of the law of substitution which Dumas has traced to so great an extent in the formation of organic compounds. When a stream of chlorine gas is transmitted through the Dutch liquor, Regnault finds that another atom of hydrogen is carried off, as hydrochloric acid, and an atom of chlorine left in its place; thus the Dutch liquor, $C_4H_3, Cl + HCl$ becomes



This second product, which is a liquid, being submitted to the action of a stream of chlorine, was found to give rise to a third liquid product, in which the hydrochloric acid of the last formula had disappeared, and the remaining portion had assumed two additional atoms of chlorine, forming—



This third liquid, is changed by the prolonged action of chlorine into the perchloride of carbon, but to hasten the action, it is convenient to conduct the operation in the light of the sun; its two atoms of hydrogen being carried off in the form of hydrochloric acid, and two atoms of chlorine left in their place, which gives the formula



Now this view of derivation and constitution of the perchloride of carbon, is confirmed by the density of its vapour

which Regnault found by experiment to be 8157. It should from its formula contain

8 volumes carbon vapour.	.	.	3371
12 volumes chlorine.	.	.	29284
			<hr/>
			32655

If these form a combining measure of 4 volumes, the most usual of all combining measures, the weight of 1 volume or density of the vapour is 8164, which almost coincides with the experimental result.*

The perchloride of carbon is a volatile crystalline solid, having an aromatic odour resembling that of camphor, fusible at 320° and boiling at 360° (Faraday), of sp. gr. 2, soluble in alcohol ether and oils. It was prepared by Faraday by exposing the Dutch liquid to sunlight in an atmosphere of chlorine, which was several times renewed, as the chlorine was absorbed.

Protochloride of carbon, C₄Cl₄.—This compound was prepared by Mr. Faraday by passing the vapour of the perchloride through a glass tube filled with fragments of glass, and heated to redness. A great quantity of chlorine becomes free, and a colourless liquid is obtained, which when purified from perchloride of carbon and chlorine as much as possible, boils at 248° (Regnault), has a sp. gr. of 1.5526, and in its chemical relations is very analogous to the perchloride of carbon. The density of the vapour of the protochloride decides the nature of its constitution. It was found by Regnault to be 5820, which corresponds to the composition by volume:—

8 volumes carbon vapour.	.	.	3371
8 volumes chlorine.	.	.	19523

22894

$$\text{Density} = \frac{22894}{4} = 5724.$$

It must, therefore, contain 4 atoms of carbon and 4 of chlorine, and its formula be C₄Cl₄, or we have come at last to olefiant gas C₄H₄ with its *whole* hydrogen replaced by chlorine.

* Regnault; De l'Action du Chlore sur la liqueur des Hollandais et sur le Chlorure d'Aldéhydène. An. de Ch. et de Ph. t. 69, p. 151. Idem, Sur les Chlorures de Carbon, ib. t. 70. p. 104.

It is interesting to observe how a body retains, after so many mutations, such distinct traces of its origin. From its analysis it might be a compound of single equivalents, C Cl , of the simplest nature, and so it was considered when named protochloride of carbon, but there have been found in it the 4 C of alcohol, to which compound we can trace it back, by many steps but with perfect certainty.

Subchloride of carbon.—Another compound of this class exists, of which a specimen produced accidentally was examined by Messrs. Phillips and Faraday. Regnault has formed it, by making the preceding liquid compound pass several times through a tube at a bright red heat. It condenses in the coldest parts of the tube in very fine silky crystals, which may be taken up by ether, and obtained perfectly pure by a second sublimation. The analysis of this substance proves that its elements are in the proportion of 2 equivalents of carbon to 1 of chlorine, but the number of its equivalents is indeterminate, as its density is unknown. If it belongs to the foregoing series, its formula will be C_4Cl_2 .

Chlorocarbonic acid gas, CO_2Cl .—This gas is made by exposing equal measures of chlorine and carbonic oxide to sunshine, when rapid but silent combination ensues, and they contract to one half their volume. It is decomposed by water, hydrochloric and carbonic acids being formed, and does not combine with bases to form salts. It belongs to the carbonic oxide series.

Chloride of boron, B Cl_3 .—A gaseous compound of these elements was obtained by Berzelius, by transmitting chlorine over boron heated in a glass tube, and by Dumas by transmitting the same gas over a mixture of boracic acid and carbon ignited in a porcelain tube. Its density was found to be 4079 by Dumas, and it is considered a terchloride.

Chloride of silicon, Si Cl_4 .—This compound is obtained by similar processes as the last. It is a limpid and volatile liquid, boiling at 124° , and is converted by water into hydrochloric acid and silica.

Chloride of sulphur, S_2Cl_2 .—This compound was first obtained by Dr. Thomson in 1804. To prepare it, 2 or 3 ounces of flowers of sulphur may be introduced into the body of a tubulated retort and gently warmed. Dry chlorine is conducted to the sulphur, by a quill tube descending through a perforated

cork in the tubulure of the retort, and a flask may be applied to the beak of the retort to receive a small portion of the product which distils over during the operation. The chlorine is rapidly absorbed and a dark coloured dense liquid is obtained, which boils at about 280° , and has a disagreeable odour, somewhat resembling that of sea-weed, but much stronger. Rose finds that this is a solution of sulphur in a definite chloride of sulphur S_2Cl , which may be obtained pure by distilling the liquid at a moderate temperature.* This compound is capable of dissolving a very large quantity of sulphur, which may be obtained in crystals from a solution saturated at a high temperature. It is decomposed by water, and hydrochloric and hyposulphurous acids formed.

This compound also absorbs a large but indefinite quantity of chlorine. But a definite superior chloride of sulphur has lately been obtained by Rose, in combination with several metallic perchlorides.† It is a bichloride of sulphur, SCl_2 , but cannot be obtained in a separate state. When chlorine is passed over the bisulphuret of tin, the gas is absorbed, the sulphuret fuses, and a compound is formed in yellow crystals, which consists of $SnCl_2 + SCl_2$. The sulphur of the sulphuret of titanium and of the sulphurets of antimony and arsenic is converted by chlorine, in the same manner into bichloride, and the metal itself obtains the same proportions of chlorine as it had of sulphur previously, the new products also remaining in combination with each other.

Terchloride of phosphorus, PCl_3 .—This chloride, which corresponds with phosphorous acid, is obtained by passing the vapour of phosphorus over corrosive sublimate in a heated tube; a clear and volatile liquid distils over, of sp. gr. 1.45. It is capable of dissolving phosphorus; when mixed with water, it is resolved into hydrochloric and phosphorous acids.

Perchloride of phosphorus, PCl_5 .—Phosphorus takes fire spontaneously in a vessel of dry chlorine, and produces a snow white woolly sublimate, which is very volatile, rising in vapour below 212° . It is converted by water into hydrochloric and phosphoric acids. Compounds also have been formed of chlorine, sulphur and phosphorus by Rose and Serullas, to which Berzelius assigns the speculative formulæ $SCl_2 + PCl_2$ and $PS_6 + 2S_2Cl$.

* An. de Ch. et de Ph. t. 50, p. 92.

† An. de Ch. et de Ph. t. 70, p. 278.

SECTION XI.

BROMINE.

Eq. 978.31 or 78.39 ; Br ; density 5393 ; .

This element was discovered by M. Balard of Montpellier in 1826. Its name is derived from *βρωμος*, mal-odour, and was applied to it on account of its strong and disagreeable odour. Like the other members of the chlorine family, it is found principally in solution, being present in an exceedingly minute but appreciable proportion in sea water, under the form of bromide of sodium or magnesium, also in the water of the Dead Sea, and in nearly all the saline springs of Europe, of which that of Theodorshall near Kreuznach in Germany is the principal source of bromine, as an article of commerce. Although it has not been found applicable to any important purpose of utility, bromine is interesting from its chemical relations, particularly from the extraordinary parallelism in properties with chlorine which it exhibits.

Preparation.—Bromine in combination is detected by means of chlorine water, a few drops of which cause the colourless solution of a bromide to become orange yellow, like nitrous acid, by disengaging bromine, while an excess of chlorine weakens the indication, by forming a chloride of bromine which is nearly colourless. Before the application of this test, the saline water in which bromine is contained must always be greatly concentrated, and, indeed, the greater part of its salts separated by crystallization. The bromides are highly soluble and remain in the incrySTALLIZABLE liquor which is called the mother-ley, or bittern in the case of sea-water. The bromide of magnesium may lose hydrobromic acid during the farther concentration of the mother-ley, by evaporation, on which account Desfosses recommends the addition of hydrate of lime to the liquid, which throws down magnesia, and produces a bromide of calcium which may be evaporated without loss of bromine. Instead of using free chlorine, to extricate the bromine, peroxide of manganese and a little hydrochloric acid may be added to the liquid. Upon distilling, bromine is liberated and comes off completely before the liquid boils. The watery vapour which condenses in the receiver along with the bromine, contains a

portion of chloride of bromine, from which the bromine may be separated by adding barytes to the liquid, and forming a chloride of barium and bromate of barytes; evaporating the liquor to dryness, and treating with alcohol.

Properties.—Bromine condenses in the preceding process as a dense liquid under the water, the sp. gr. of bromine being 2.966. In mass, it is opaque and of a dark brown red, but in a thin stratum, transparent and of a hyacinth red. Its odour is powerful and very like that of chlorine. When cooled 10° or 15° degrees below zero, it freezes, and remains solid at 10°; it then has a leaden gray colour and a lustre almost metallic. Bromine at the usual temperature is decidedly volatile, and to retard its evaporation, it is generally covered by water in the bottle in which it is kept. It boils at 116°.5, and affords a vapour very similar to the ruddy fumes of peroxide of nitrogen. Bromine is soluble to a small extent in water, and gives an orange coloured solution; it is a little more soluble in alcohol, and considerably more so in ether.

Bromine bleaches like chlorine, and acts in a similar manner upon the volatile oils and many organic substances containing hydrogen, which element it eliminates in the form of hydrobromic acid. Many metals combine with bromine with ignition, as they do with chlorine; it acts as a caustic on the skin and stains it yellow, like nitric acid. It forms a combination with starch, which is of a yellow colour; like chlorine it forms a crystalline hydrate with water at 32°, which is of a beautiful red tint.

Hydrobromic acid, H Br.—This is a gas, in which 2 volumes of each constituent are united without condensation, as in hydrochloric acid, and which has the great attraction for water of that acid. Hydrogen and bromine do not unite at the usual temperature, and a mixture of them is not exploded by flame, but they unite in contact with the flame and form hydrobromic acid. The same acid is more readily prepared by the action of bromine upon certain compounds of hydrogen, such as sulphuretted hydrogen, phosphuretted hydrogen and hydriodic acid. The gas may also be obtained by the mutual action of bromine, phosphorus and water, and must be collected over mercury.

Hydrobromic acid, like all the other bromides, is decomposed by chlorine, which is more powerful in its affinities than bro-

mine, but it is not decomposed by iodine. Its action with metals is precisely similar to that of hydrochloric acid. Hydrobromic acid is not decomposed when heated with oxygen, and water is not decomposed by bromine, so that the affinity of bromine and oxygen for hydrogen may be inferred to be nearly equal. This acid, or a soluble bromide, produces white precipitates with the nitrates of silver, lead and suboxide of mercury, which are very similar to the chlorides of these metals. The other metallic bromides correspond in solubility with the chlorides. The bromide of silver, like the chloride, is soluble in ammonia.

Bromic acid, Br O_5 .—Bromine is dissolved by the strong alkaline bases, and occasions a decomposition exactly similar to that produced by chlorine, in which a bromide of the metal and bromate of the metallic oxide are formed. The bromic acid may be separated from bromate of barytes by sulphuric acid, and its solution may be concentrated to a certain point, like chloric acid, beyond which it undergoes decomposition. It has not been isolated. The chief points of difference between chloric and bromic acid are, that the latter alone is decomposed by sulphurous and phosphorous acids, and by sulphuretted hydrogen; and while all the chlorates are soluble, it is said, that the bromates of silver and suboxide of mercury are insoluble, the former being a white and the latter a yellowish white precipitate. Bromic acid is the only known oxide of bromine.

Chloride of bromine, Br Cl_5 .—Chlorine gas is absorbed by bromine, and a volatile fluid of a reddish yellow colour produced. This chloride appears to dissolve in water without decomposition, but in an alkaline solution, it is converted into chloride and bromate.

Bromide of sulphur.—Bromine combines when mixed with flowers of sulphur, forming a fluid of an oily appearance and reddish tint, much resembling chloride of sulphur in appearance and properties. This bromide dissolves both sulphur and bromine, and has not been obtained in a state of sufficient purity for analysis.

Bromides of phosphorus, P Br_3 and P Br_5 .—If bromine and phosphorus are brought into contact in a flask filled with carbonic acid gas, a violent action with ignition takes place, of which the products are a volatile crystalline solid, and a yellowish liquid. The former, when decomposed by water, affords

hydrobromic and phosphoric acids, which proves it to be P Br_5 ; and the latter affords hydrochloric and phosphorous acids, which proves it to be P Br_3 . The liquid bromide does not freeze at 5° , and like the liquid chloride of phosphorus is capable of dissolving a large quantity of phosphorus.

Bromide of carbon.—It is probable that the compound described as such by Serullas is *bromoform*, $\text{C}_2 \text{H Br}_3$.*

Bromide of silicon—Is prepared by a similar process as the chloride of silicon. It is a liquid boiling at 302° and freezing at 10° . By water it is resolved into hydrobromic acid and silica.

SECTION XII.

IODINE.

Eq. 1579.5 or 126.57 ; I ; *density* 8707.7 ; .

Iodine was discovered in 1811, by M. Courtois of Paris, in kelp, a substance from which he prepared carbonate of soda. Its chemical properties were examined by Clement, and afterwards, more completely by Davy and Gay-Lussac, particularly the latter.† A trace of iodine has been observed in sea-water (Schweitzer), but it is more abundant in the fuci, ulvi and other marine plants, and also in sponge, the ashes of which contain iodide of sodium. It is known also to exist in one mineral, a silver ore of Albaradon in Mexico. Iodine has not as yet, I believe, found any important application in the useful arts, but it has proved a valuable addition to the materia medica.

Preparation.—The greater part of the iodine of commerce is prepared at Glasgow from the kelp of the west coast of Ireland, and western islands of Scotland. The sea-weed thrown upon the beach is collected, dried, and afterwards burned in a shallow pit, in which the ashes accumulate and melt by the heat, being of a fusible material. The fused mass broken into lumps forms kelp, which was prepared and chiefly valued at one time for the carbonate of soda it contains, which varies in quantity from 2 to 5 per cent. It is not all equally rich in iodine. According to the observation of Mr. Whitelaw, the long elastic stems of the fucus palmatus afford most of the iodine contained in kelp,

* An. de Ch. et de Ph. t. 39, p. 225.

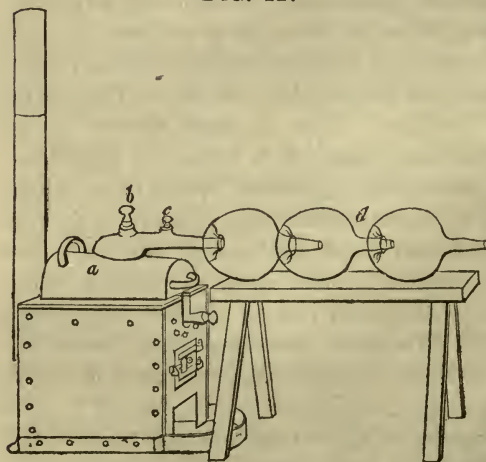
† Davy in Philosophical Transactions for 1814 and 1815 ; Gay-Lussac in the Annales de Chimie, t. 88, 90 and 91.

and the kelp prepared from this plant may be recognized by the presence of charred portions of the stems; and as that is a deep sea plant, it is found in largest quantity in the sea-wreck of exposed coasts. A high temperature in the preparation of the kelp, which increases the proportion of alkaline carbonate, diminishes that of the iodine, owing to the volatility of the iodide of sodium at a full red heat. The kelp which contains most iodine, generally contains also most chloride of potassium, and it is for these two products that the substance is now valued, more than for its alkali.

The kelp broken into small pieces is lixiviated in water, to which it yields about half its weight of salts. The solution is evaporated down in an open pan, and when concentrated to a certain point, begins to deposit its soda salts, namely, common salt, carbonate and sulphate of soda, which are removed from the boiling liquor by means of a shovel pierced with holes like a colander. The liquid is afterwards run into a shallow pan to cool, in which it deposits a crop of crystals of chloride of potassium; the same operations are repeated upon the mother-ley of these crystals until it is exhausted. A dense dark-coloured liquid remains, which contains the iodine, in the form, it is believed, of iodide of sodium, but mixed with a large quantity of other salts, and this is called the iodine ley.

To this ley, sulphuric acid is gradually added in such quantity as to leave the liquid very sour, which causes an evolution

FIG. 42.



of carbonic acid, sulphuretted hydrogen, and sulphurous acid gases, with a considerable deposition of sulphur. After standing for a day or two, the ley so prepared, is heated with peroxide of manganese, to separate the iodine. This operation is conducted in a leaden retort *a* (see figure) of a cylindrical form, supported in a sand-

bath, which is heated by a small fire below. The retort has a large opening, to which a capital *b c*, resembling the head of an alembic, is adapted, and luted with pipe-clay. In the capital itself there are two openings, a larger and a smaller, at *b* and *c*, closed by leaden stoppers. A series of bottles *d*, having each two openings, connected together as represented in the figure, and with their joinings luted, are used as condensers. The prepared ley being heated to about 140° in the retort, the manganese is then introduced, and *b c* luted to *a*. Iodine immediately begins to come off, and proceeds on to the condensers, in which it is collected; the progress of its evolution is watched by occasionally removing the stopper at *c*; and additions of sulphuric acid or manganese are made by *b*, if deemed necessary. The success of the experiment depends much upon its being slowly conducted, and upon the proper management of the temperature, which is more easily regulated when the quantities of materials are considerable, than when the experiment is attempted with small quantities in glass flasks. In the latter circumstances, chlorine is often evolved with the iodine, which escapes in acrid fumes, as the chloride of iodine, and is lost; but this accident can be avoided in the manufacturing process. A little cyanide of iodine often accompanies the iodine, which being more volatile, condenses in the form of white, flexible, prismatic crystals, in the bottle most distant from the leaden retort.

In this operation, the peroxide of manganese will be in contact at once with hydriodic, hydrochloric and sulphuric acids; and the iodine of the hydriodic acid may be liberated, from the union with its hydrogen of the oxygen of the manganese, and the formation of water; or hydrochloric acid may be first decomposed by the manganese, and chlorine decompose the hydriodic acid and liberate iodine. If a considerable excess of sulphuric acid be employed, iodine is obtained without the use of the peroxide of manganese, the oxygen required by the hydrogen of the hydriodic acid being supplied by the sulphuric acid, a part of which is converted into sulphurous acid. The presence of iodine in the prepared ley may be observed by suddenly mixing it with an equal volume of oil of vitriol, when violet fumes of iodine appear. But the quantity of iodine may be more accurately estimated by means of a solution consisting of 1 part of crystallized sulphate of copper and $2\frac{1}{4}$ cr. proto-

sulphate of iron, which throws down an insoluble subiodide of copper, almost white.

Properties.—Iodine is generally in crystalline scales of a bluish black colour and metallic lustre. It may also be obtained, from solution, in the form of elongated octohedrons with a rhomboidal base. The density of iodine is 4.948; it fuses at 225°, and boils at 347°; but it evaporates at the usual temperature, and more rapidly when damp than when dry, diffusing an odour having considerable resemblance to chlorine, but easily distinguished from it. Iodine stains the skin of a yellow colour, which however disappears in a few hours. Its vapour is of a splendid violet colour, which is seen to great advantage when a scruple or two of iodine is thrown at once upon a hot brick. Hence its name, from *ἰώδης*, violet-coloured. The vapour of iodine is the heaviest of gaseous bodies, its density being 8716 according to the experiment of Dumas, and 8707.7 according to calculation from its atomic weight.

Pure water dissolves about 1-7000th of its weight of iodine, and acquires a brown colour; but when charged with a salt, particularly the nitrate or hydrochlorate of ammonia, water dissolves a considerably greater quantity of iodine. The solution of iodine does not disengage oxygen in the light of the sun, and does not destroy vegetable colours, but after a time it becomes colourless, and then contains hydriodic and iodic acids. In other respects, iodine generally comports itself like chlorine, but its affinities are much less powerful. Iodine is soluble in alcohol and ether, with which it forms dark reddish brown liquors. Solutions of iodides, too, all dissolve much iodine. A liquid containing 20 grains of iodine and 30 grains of iodide of potassium in 1 ounce of water, is known as Lugol's solution, and preferred to the tincture in medicine, because the iodine is not precipitated from it by dilution with water.

A solution of starch forms an insoluble compound with iodine, of a deep blue colour, the production of which is an exceedingly delicate test of iodine. If the iodine be free, starch produces at once the blue precipitate, but if it be in combination as a soluble iodide, no change takes place, till chlorine is added to liberate the iodine. If more chlorine, however, be added than is necessary for that purpose, the iodine is withdrawn from the starch, chloride of iodine formed, and the blue compound destroyed. Dr. A. T. Thomson, after adding the starch with a

drop of sulphuric acid to the liquid containing an iodide, in a cylindrical vessel, allows the vapour only from the chlorine-water bottle to fall upon the solution, and not the chlorine-water itself. In this way, the danger of adding an excess of chlorine is easily avoided, and the test indicates in a sensible manner an exceedingly minute quantity of iodine. The iodide of starch, in water, becomes colourless when heated, but recovers its blue colour if immediately cooled. The soluble iodides give, with nitrate of silver, an insoluble iodide of silver, of a pale yellow colour, insoluble in ammonia; with salts of lead, an iodide of a rich yellow colour, and with corrosive sublimate, a fine scarlet iodide of mercury.

In ascertaining the quantity of iodine in the mixed chlorides, and iodides of mineral waters and other solutions, Rose recommends the addition of nitrate of silver, which throws down a mixture of chloride and iodide of silver, which is fused and weighed. This is afterwards heated in a tube and chlorine passed over it, by which the iodine is expelled, and the whole becomes chloride of silver. It is weighed again, and a loss is found to have occurred, owing to the equivalent of the replacing chlorine being less than that of the replaced iodine. This loss, multiplied by 1.389, gives the quantity of iodine originally present, which has been expelled by the chlorine.* Dr. Schweitzer employs a similar method in estimating the quantity of iodine when mixed with bromine, heating the iodide and bromide of silver in an atmosphere of bromine. The difference in weight multiplied by 2.627 gives the proportion of iodine, and multiplied by 1.627 the proportion of bromine.†

Uses.—Iodine is employed in the laboratory for many chemical preparations, and as a test of starch. It was first introduced into medicine by Coindet of Geneva, who employed it with success, in the treatment of goitre, dissolved in alcohol, in solution of iodide of potassium, or as iodide of sodium; and since that application, most mineral waters to which the virtue of curing goitre was ascribed, have been found to contain iodine. M. Boussingault has adduced striking confirmations of the efficacy of iodine in that disease, in his interesting memoir

* Handbuch der analytischen Chemie von Heinrich Rose, B. 2, p. 577, Berlin, 1838.

† Phil. Mag. 3rd. series, v. 15, p. 57.

on the iodiferous mineral waters of the Andes.* It appears to have a specific action in causing the absorption of glandular swellings, and is also administered as a tonic. Iodine swallowed in the solid state may cause ulceration of the mucous membrane of the stomach, and death. But the iodide of potassium or sodium is not poisonous in large doses, nor is the iodide of starch hurtful (Dr. A. Buchanan).

Iodides.—Iodine does not form a hydrate like chlorine, but it combines with another compound body, ammonia; dry iodine absorbing dry ammoniacal gas and running into a brown liquid, which Bineau finds to contain 20.4 ammonia for 100 iodine, quantities in the proportion of 3 equivalents of ammonia to 2 of iodine.† This liquid dissolves iodine. Iodine does not combine with dry iodide of potassium, but with the addition of a small quantity of water, it forms what appears to be a ternary compound of iodide of potassium, water and iodine, which is fluid, but was obtained in crystals by Bauer. It forms similar combinations with other hydrated metallic iodides. With the metals generally iodine combines, with the same facility, and nearly with as much energy as chlorine does. The iodide of zinc and protiodide of iron, which are very soluble, are formed by simply bringing the metals into contact with iodine, in water. All the iodides are decomposed by bromine, as well as by chlorine.

The compounds of iodine may be shortly described in the following order:

Hydriodic acid . . .	H I	Iodide of sulphur
Iodic acid . . .	I O ₅	Iodides of phosphorus
Hyperiodic acid . .	I O ₇	Chlorides of iodine.
Iodide of nitrogen	N I ₃	Bromides of iodine.

COMPOUNDS OF IODINE.

Hydriodic acid, H I.—Hydriodic acid cannot be prepared with advantage by treating the iodide of sodium or potassium with hydrated sulphuric acid, as the latter is partially converted into sulphurous acid by hydriodic acid, with the separation of iodine. It may be obtained in the state of gas, by forming an iodide of phosphorus, 9 parts of dry iodine and 1 of phosphorus being introduced into a tube sealed at one end, to be used as a retort,

* An. de Ch. et de Ph. t. 54, p. 163. † An. de Ch. et de Ph. t. 67, p. 226.

and the mixture covered by pounded glass, and combination determined by a gentle heat; and afterwards decomposing this iodide of phosphorus by a few drops of water. Hydriodic acid instantly comes off as gas, and hydrated phosphorous acid remains in the tube. Or PI_3 and $6\text{H O} = 3\text{H I}$ and $3\text{H O} + \text{P O}_3$. A slight heat may be applied to the tube, when the action abates, to expel the last portions of hydriodic acid; but if the temperature be elevated, the residuary hydrated phosphorous acid is decomposed with the evolution of phosphuretted hydrogen gas, which may, therefore, be obtained by the same operation. This gas is very soluble in water, and soon decomposed over mercury, which combines with its iodine and liberates hydrogen, so that it ought to be collected by the method of displacement. The gas is conducted by a tube to the bottom of a dry bottle, the air of which it displaces, as in the experiment with hydrochloric acid (figure, page 355), and the bottle is closed with a glass stopper when full of gas. Hydriodic gas is colourless, of density 4443 by experiment and 4385 by theory, and consists of 2 volumes of iodine vapour and 2 volumes of hydrogen gas united without condensation, or forming 4 volumes, which are, therefore, the combining measure of the gas. In the combination of its constituents by volume, hydriodic acid resembles hydrochloric gas and all the other hydrogen acids. Hydriodic gas is gradually decomposed by oxygen, with the formation of water; iodine is liberated.

The solution of this acid in water may be obtained by transmitting sulphuretted hydrogen gas through water in which iodine is suspended; the iodine combines with the hydrogen of that compound and liberates the sulphur. The liquid may afterwards be warmed to expel the excess of sulphuretted hydrogen, and filtered. It is colourless at first, but in a few hours becomes red, owing to the decomposition of hydriodic acid by the oxygen of the air, and the solution of the iodine in the acid. The solution has its maximum boiling point, which lies between 257° and 262° , when of sp. gr. 1.7, according to Gay-Lussac. Nitric and sulphuric acids decompose it, and are decomposed themselves, with the formation of water; the starch test then indicates free iodine.

Iodic acid, IO_5 .—Iodine does not afford a peculiar acid compound, with red oxide of mercury and those metallic oxides which yield hypochlorous acid with chlorine. Nor is it absorbed,

like chlorine, by hydrate of lime or alkaline solutions, to form a class of bleaching salts. Such compounds are wanting in the series of oxides of iodine, which is at present limited to iodic and hyperiodic acids. Sementini imagined that he had formed inferior oxides of iodine, but he is evidently mistaken. The iodate of soda combines with iodide of sodium in several proportions, one of which was supposed by Mitscherlich, when he discovered it, to be an iodate of soda, but that this is a double salt of the constitution first mentioned is now beyond doubt.

A few grains of iodic acid may easily be prepared by the method of Mr. Connel, which consists in heating the most concentrated nitric acid upon a little iodine, in a wide glass tube, and afterwards evaporating to dryness by a heat not exceeding 4 or 500°; a white crystalline powder remains in the tube, which is anhydrous iodic acid. When a larger quantity is required, the most convenient process is to form, in the first place, an iodate of soda. An ounce or two of iodine may be suspended in a pound of water, with occasional agitation, and a stream of chlorine be passed through, till the whole iodine is dissolved. Carbonate of soda is added to the liquor, which is of a brown colour and strongly acid, till it becomes slightly alkaline, when a large precipitation of iodine occurs, which may be separated and collected on a filter. This iodine may be suspended in water and exposed to a stream of chlorine as before. But the filtered solution contains iodate of soda and chloride of sodium, with a trace of carbonate, which may be neutralized by hydrochloric acid. On afterwards adding chloride of barium to the filtered solution, so long as a precipitate is produced, the whole iodic acid will be thrown down as iodate of barytes, which may be collected on a filter and dried. This iodate is anhydrous, and may be decomposed completely, by boiling 9 parts of it for half an hour with 2 parts of oil of vitriol, diluted with 10 or 12 parts of water. The liberated iodic acid dissolves, and being separated from the sulphate of barytes by filtration, is obtained as an anhydrous crystalline mass when evaporated to dryness by a gentle heat.

Iodic acid crystallizes from a strong solution, as a hydrate, in large and transparent crystals, which are six-sided tables. This acid is not sublimed, but decomposed, by a high temperature, and leaves no solid residue. Iodic acid is very soluble; and

after reddening, bleaches litmus paper. It oxidates all metals with which it has been tried, except gold and platinum. It is deoxidized by sulphurous acid, and iodine liberated, but an excess of sulphurous acid causes the iodine again to disappear as hydriodic acid, water being decomposed by the simultaneous action of sulphurous acid and iodine upon its elements. Morphia is said to be the only vegetable alkali which decomposes iodic acid and liberates iodine; and, hence, iodic acid has been recommended as a test for morphia.

Iodates.—The salts of iodic acid have a general resemblance to the chlorates. The iodate of potash is converted by heat into iodide of potassium and oxygen; but the iodate of soda loses iodine as well as oxygen, when heated, and a yellow, sparingly soluble, alkaline matter remains, which Liebig imagines to contain the salt of an iodous acid, resolvable into an iodate and iodide by solution in water, but which requires further investigation. The iodates of metallic protoxides, with the exception of the potash family, are all sparingly soluble or insoluble salts. The iodate of lime contains water, and when heated affords no iodide of calcium, but caustic lime.

Fixed acids, which have little affinity for water, such as iodic acid, appear often to combine in several proportions with oxides of the potash family. The ordinary biniodate of potash contains, I find, an atom of basic water, but at a high temperature it is made anhydrous, and then a salt remains containing two atoms of acid to one of potash. Mr. Penny has crystallized a biniodate and teriodate of soda, both anhydrous.

Iodic acid likewise combines with other acids, an observation of Davy's, which was disputed, but has been confirmed by Berzelius.* These are compounds which generally precipitate in a crystalline form, when another acid is added to a hot and concentrated solution of iodic acid. Compounds of sulphuric, nitric, phosphoric and boracic acids with iodic acid were formed by Berzelius. The compound with sulphuric acid may be sublimed without decomposition. When vegetable acids are dissolved in iodic acid, they are immediately decomposed by it, carbonic acid being disengaged with effervescence and iodine precipitated.

Hyperiodic or Periodic acid, I O_7 .—This acid, which was

* *Traité de Chimie*, t. I. p. 212.

discovered by Magnus and Ammermuller, is formed by transmitting a current of chlorine through a solution of iodate of soda, to which, at least, three times as much caustic soda has been added as there is of soda in the iodate. Two salts are formed, the chloride of sodium and a hyperiodate of soda with excess of soda, which is sparingly soluble, and precipitated by nitrate of silver, which throws down a sub-hyperiodate of silver. This salt may be washed, and afterwards dissolved in nitric acid, and the solution evaporated yields orange-yellow crystals of neutral hyperiodate of silver. It is remarkable that when these crystals are thrown into water they are decomposed, the whole oxide of silver precipitating with half the hyperiodic acid, as the former insoluble sub-hyperiodate, while half the acid is dissolved by the water without a trace of silver, and obtained in a state of purity. This solution when evaporated affords hyperiodic acid in crystals, which are unalterable in the air, and of which the solution in water is not changed by ebullition. The solution, treated with hydrochloric acid, affords chlorine and iodic acid, water being formed. Hyperiodic acid is resolved into oxygen and iodine by a high temperature.

Hyperiodates.—Besides neutral salts of this acid, subsalts of the potash family exist which contain two of base to one of acid. If these are subsalts they are unique, as no true subsalts of the potash family are known. But it is more probable that hyperiodic acid forms a second and bibasic class of salts, to which they belong.*

Iodide of nitrogen.—Iodine has an action similar to that of chlorine upon ammonia, and forms when digested in a solution of that substance, an insoluble black powder, which is powerfully detonating, and analogous to the chloride of nitrogen. The iodide detonates more easily, but less violently than the chloride, always exploding spontaneously when it dries. Another process is to mix a great excess of ammonia, with a saturated solution of iodine in alcohol, and afterwards to add water so long as iodide of nitrogen precipitates. The filter with the humid precipitate should be divided into several pieces, otherwise the whole may explode, at once, upon drying. The same obscurity hangs over the composition and constitution of the iodide as the chloride of nitrogen.

* Poggendorff's *Annalen*, vol. 28, p. 514.

When caustic soda is added to the solution of iodine in alcohol or wood-spirit, a yellow substance of a saffron odour precipitates, which was supposed by Mitscherlich to be the periodide of carbon, but is *iodoform*, of which the formula is $C_2H I_3$. No true iodide of carbon is known.

Iodide of sulphur.—This compound is formed by fusing together 4 parts of iodine and 1 of sulphur. It has a radiated crystalline structure, but its elements are easily disunited, the iodine escaping entirely from this compound when it is left exposed in the air.

Iodides of phosphorus.—Iodine appears to combine with phosphorus in several proportions, when they are brought in contact and slightly heated. In all these combinations, the mass becomes hot without inflaming, if the phosphorus is not at the same time in contact with air. One part of phosphorus with 6, 12 and 20 parts of iodine forms fusible solids, which may be sublimed without change, but which are decomposed by water, all of them yielding hydriodic acid, and the first affording besides phosphorus and phosphorous acid, the second phosphorous acid, and the third phosphoric acid.

Chlorides of iodine.—Chlorine is readily absorbed by dry iodine and perhaps more than one compound formed. Berzelius forms a definite compound by distilling a mixture of 1 part of iodine with 4 parts or more of chlorate of potash. There is formed in the retort, a mixture of iodate and hyperchlorate of potash, at the same time that oxygen gas is disengaged, and a chloride of iodine is formed which condenses in the receiver. This chloride of iodine is a yellow or reddish liquid, of an oily consistency, of a sharp and peculiar odour, and of a taste which is feebly acid, but very astringent and rough. It is soluble in water and alcohol; and ether extracts it from its aqueous solution unaltered, so that it is not decomposed by solution in water. It is supposed to consist of single equivalents of chlorine and iodine.*

When iodine is completely saturated with chlorine, it forms a compound which is solid and yellow, fusible by heat, but which cannot be sublimed without loss of chlorine. It fumes in air and has an acrid odour. It is decomposed by water and forms a colourless solution, which consists of hydrochloric and iodic acids. This proves the composition of this iodide to be

* Berzelius, *Traité de Chimie*, t. 1, p. 110.

$I Cl_5$. When treated in the dry state with anhydrous alcohol or ether, these menstrua take up hydrochloric acid and chloride of iodine, leaving iodic acid white and pulverulent.

Bromides of iodine.—Iodine likewise forms two bromides, which are both soluble in water. The solution bleaches litmus paper without first reddening it.

SECTION XIII.

FLUORINE.

Eq. 233.8 or 18.74; F; *density (hypothetical)* 1292; $\square\square$.

This elementary body is most frequently found in the mineral kingdom in combination with calcium, or as fluoride of calcium, which constitutes the mineral, fluor spar, and exists in small quantity in amphibole, mica and most of the natural phosphates; a trace of it also occurs in the enamel of the teeth, and in the bones of animals. Of all bodies, fluorine appears to possess the most powerful and general affinities, and to be, therefore, the most difficult to isolate, or to preserve for the study of its properties. Indeed we have hitherto learned little more of fluorine than that it exists and may be isolated. Several of its compounds, however, are of less difficult preparation and well known.

Sir H. Davy made several attempts to isolate fluorine. He exposed the fluoride of silver in a glass tube to gaseous chlorine, at a high temperature, and found that chloride of silver was produced, and fluorine therefore liberated, but it was absorbed and replaced by oxygen, which it disengaged from the silica and soda of the glass. When Davy repeated the same experiment in a platinum vessel, the metal became covered with fluoride of platinum. He proposed afterwards to construct vessels of fluor spar for the reception of the fluorine, which he expected to disengage from the fluoride of phosphorus by burning it in oxygen gas; but he does not appear to have carried this project into execution, and it is to be feared that any such operation, in which an excess of chlorine is necessarily employed, would yield a chloride of fluorine, rather than pure fluorine. M. Baudrimont avoided the use of chlorine, and transmitted the volatile fluoride of boron over deutoxide of lead (minium) in an ignited porcelain

tube. Having obtained a gas, supposed to be fluorine, which did not act upon glass, mixed with much oxygen, he substituted for this, another operation quite analogous to the usual process for chlorine. Oil of vitriol was heated upon a mixture of fluor spar and peroxide of manganese, in a glass retort. The gaseous product was believed to be a mixture of hydrofluoric and fluosilicic acids with fluorine vapour, which were not separated from each other, but the latter is described as a gas of a yellowish brown colour, having an odour resembling chlorine and burnt sugar, and capable of bleaching. Fluorine did not act upon glass, but combined at once with gold. The Messrs. Knox have obtained similar results.* But more than one skillful chemist of name has been less fortunate in obtaining indications so decisive of the isolation of fluorine.

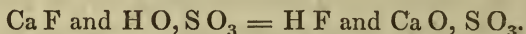
Hydrofluoric acid, H F. Schwankhardt, of Nuremberg, observed in 1670, that it was possible to etch upon glass by means of fluor spar and sulphuric acid, but it was not till 1771 that Scheele referred this action to a particular acid which sulphuric acid disengaged from fluor spar. Wenzel first obtained the true hydrofluoric acid, exempt from silica, by preparing it in proper metallic vessels, the acid collected by Scheele being the fluosilicic and not the hydrofluoric. The preparation and properties of the pure acid were more fully studied by Gay-Lussac and Thenard in 1810. It was then known as fluoric acid, and was supposed, according to the doctrine of the day, to contain oxygen. The idea of its being a hydrogen acid was first suggested, a few years afterwards, by M. Ampère, whose views in theoretical chemistry were often marked by much acuteness and originality. The view of Ampère is now generally assented to, although from our imperfect knowledge of fluorine, the constitution of hydrofluoric acid does not rest upon the same indisputable evidence as that of hydrochloric acid, to which it is assimilated.

Preparation.—To obtain hydrofluoric acid anhydrous, a specimen of fluor spar is selected free from siliceous minerals and galena; this is reduced to an impalpable powder and distilled by a gentle heat in a retort of lead, with twice its weight of highly concentrated oil of vitriol. The materials become viscid and

* Baudrimont, Phil. Mag. 3rd series, v. 10, p. 149; G. J. and the Rev. T. Knox, Ib. vols. 9, p. 107 and 12, 105.

swell considerably, and an acid vapour distils over, which is even more acrid and suffocating than chlorine, and produces severe sores if allowed to condense upon the hands of the operator. This vapour is received in a flask or bottle, likewise of lead, kept cold by ice, in which it condenses without the presence of water. The acid, thus obtained, may be preserved in vessels of platinum or gold, provided with stoppers of the same metal which fit accurately, or in vessels of lead formed without tin solder, tin being rapidly acted upon by hydrofluoric acid. If the solution of this acid in water is required, the extremity of the leaden tube, from the retort, may be allowed to touch the surface of water in a platinum crucible or capsule, by which the acid vapour is readily condensed; and the dilute acid may be preserved without much contamination in a glass bottle, which has been previously heated and coated internally with melted bees-wax.

Fluor spar, which is employed in this operation, is the fluoride of calcium, upon which the action of hydrated sulphuric acid is similar to its action upon chloride of sodium, in which hydrochloric acid is produced. Water is decomposed, by the hydrogen and oxygen of which, the fluorine and calcium are converted respectively into hydrofluoric acid and lime; and the former comes off as vapour, while the latter remains in the retort as sulphate of lime. In symbols:



Water is, therefore, necessary to the formation of hydrofluoric acid in the process given for its preparation; and the observation of M. Kuhlman, that anhydrous sulphuric acid vapour has no action upon fluor spar at a high temperature, is readily accounted for. Did fluor spar contain an oxygen acid, in combination with lime, the acid should be equally liberated by the anhydrous or hydrated sulphuric acid.

Properties.—Anhydrous hydrofluoric acid is a colourless, fuming and very volatile liquid, boiling not much above 60° ; and which does not freeze at 4° . Its sp. gr., which is 1.0609, is increased to 1.25 by the addition of a certain quantity of water, for which it has an intense affinity. Hydrofluoric like hydrochloric acid, dissolves the more oxidable metals with the evolution of hydrogen gas. Mixed with nitric acid, it dissolves ignited silicon and titanium, with disengagement of nitric oxide;

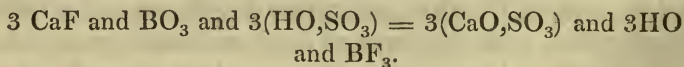
but that acid mixture has no action upon the noble metals, such as gold and platinum, which are dissolved by aqua regia. Several insoluble acid bodies, which are not acted on by sulphuric, nitric or hydrochloric acid, are dissolved with facility by hydrofluoric acid; such as silica, titanite, tantalite, molybdic and tungstic acids. Water is then formed from the oxygen of these acids and the hydrogen of hydrofluoric acid, and fluorides of silicon or of the metals of the acids enumerated are likewise produced; which fluorides appear to combine with undecomposed hydrofluoric acid, when water is present. This acid destroys glass by acting upon its silica. If a drop of the concentrated acid be allowed to fall upon a glass plate, it becomes hot, enters into ebullition and volatilizes in a thick smoke, leaving the spot with which it was in contact deeply corroded, and covered by a white powder composed of the elements of the glass excepting a portion of the silica, which has passed off as gaseous fluoride of silicon.

The diluted solution, or the vapour of hydrofluoric acid is sometimes used to etch upon glass. The purity of the acid being of little moment in this application of it, the sulphuric acid and fluor spar may be mixed in a stone-ware evaporating basin. The glass is warmed sufficiently to melt bees' wax rubbed upon it, and thereby covered with a coating of that substance, which is afterwards removed from the parts to be etched, by a pointed rod of lead or tin, employed as a graver. A gentle heat being applied to the basin, acid fumes are evolved to which the etched surface of the glass is exposed for a minute or two, care being taken not to melt the wax. The wax is afterwards removed by warming the glass, and wiping it with tow and a little oil of turpentine, when the exposed lines are found engraved to a depth proportional to the time they have been exposed to the acid fumes. But in taking impressions upon paper from glass plates engraved in this way, as from a copper-plate, they are too apt to be broken from the pressure applied in printing.

To detect the minute quantity of hydrofluoric acid, which exists in many minerals, Berzelius recommends that the substance to be examined be reduced to fine powder and mixed with concentrated sulphuric acid, in a platinum crucible covered by a small plate of glass, waxed and engraved as described. The crucible is then exposed to a gentle heat, insufficient to melt the wax, and in half an hour, the glass plate may be removed

and cleaned. If the mineral submitted to the test contained fluorine, the design will be perceived upon the glass; when the quantity of fluorine, however, is very small, the engraving does not appear immediately, but becomes visible on passing the breath over the glass. The presence of silica in the mineral interferes with this operation, but an indication may then be obtained by heating a fragment of the mineral to redness upon a piece of platinum foil slipt into a glass tube, 8 or 10 inches in length and open at both ends. The tube is held obliquely with the mineral near the lower end, and so that part of the vapour from the flame passes up the tube. The moisture, thus introduced, carries away the gaseous fluoride of silicon, and condenses in drops in the upper part of the tube. These drops when afterwards evaporated, in drying the tube, leave a white spot, which consists of silica, coming from the decomposition of the fluoride of silicon by the water with which it condensed. (Berzelius). Dr. G. O. Rees has lately called in question the existence of fluorine in bones, which he finds, contrary to the general opinion, not to be indicated in them by this test.

Fluoride of boron, fluoboric acid, BF_3 .—This compound is gaseous, and is obtained when dry boracic acid is brought in contact with concentrated hydrofluoric acid; when boracic acid is ignited with fluor spar; and most conveniently by heating together in a glass retort, 1 part of vitrified boracic acid, 2 of fluor spar and 12 of concentrated sulphuric acid, although this process does not give it free from fluosilicic acid. The reaction by which the fluoboric acid is then produced may be thus expressed:



Fluoboric gas has no action upon glass, and may be collected in glass vessels over mercury. It is colourless, but produces thick fumes when allowed to escape into the atmosphere. Its density according to Dr. J. Davy is 2371, and 2312 according to Dumas, who finds 1 volume of this gas to contain $1\frac{1}{2}$ vol. of fluorine. Fluoboric gas is not decomposed by iron and the ordinary metals, even at a bright red heat, but on the contrary, potassium, with the metals of the alkalies and alkaline earths, decomposes it at a red heat; boron is liberated by potassium, and a double fluoride of boron and potassium also formed.

Water absorbs fluoboric acid gas with the greatest avidity, taking up, according to J. Davy, 700 times its volume, which increases its bulk considerably and raises its density to 1.77. The most ready mode of preparing the solution of this acid, is to dissolve crystallized boracic acid in hydrofluoric acid. The acid is extremely caustic and corrosive, charring and destroying wood and organic matters, when concentrated, like sulphuric acid, probably from its avidity for moisture.

A dilute solution of fluoride of boron, undergoes spontaneous decomposition, according to Berzelius, depositing one fourth of its boron in the form of boracic acid, which crystallizes at a low temperature; while a compound of hydrofluoric acid and fluoride of boron remains in solution, which he terms *hydrofluoboric acid*. The fluoride of boron has a great disposition to form double fluorides, and acts upon basic metallic oxides like the following compound.

Fluoride of silicon, fluosilicic acid, Si F_3 .—This gas is obtained in the following manner: equal parts of fluor spar and broken glass or quartz sand, in fine powder, are mixed in a

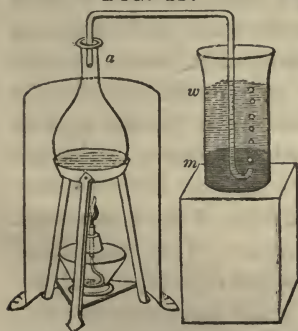


FIG. 43. glass flask *a* (figure 43), to be used as a retort, with six parts of concentrated sulphuric acid, and stirred well together. A disengagement of gas immediately takes place, and the mass swells up considerably, so that the flask must be capacious. After a time, a gentle heat is required to aid the operation. Fluosilicic gas is collected over mercury. In its physical characters it resembles fluoboric gas. Its

density is 3574 according to J. Davy, and 3600 according to Dumas; it contains twice its volume of fluorine. In transmitting this gas into water, the tube must not dip in the fluid, for it would speedily be choked by the deposition of silica, produced by the action of water upon the gas. In the arrangement figured, the extremity of the exit tube is covered by a small column of mercury *m*, in the lower part of the jar, through which the gas passes before it reaches the water *w*. Every bubble of gas exhibits a remarkable phenomenon, as it enters the water, becoming invested with a white bag of silica, which rises to the surface. It often happens, in the course of the operation, that

the gas forms tubes of silica, in the water, through which it gains the surface without decomposition, if they are not broken from time to time. When water is completely saturated with the fluoride of silicon, it has taken up about once and a half its weight, and is a gelatinous, semi-transparent mass, which fumes in the air. The liquid contains two equivalents of water to one of the original fluoride of silicon; but one third of the fluoride has been decomposed by the water and converted into hydrofluoric acid and silica. The hydrofluoric acid and fluoride of silicon, in solution, are supposed to be in combination by Berzelius, forming $3\text{HF} + 2\text{Si F}_3$, which is termed by him *hydrofluosilicic acid*. When this liquid is placed in a moderately warm situation, the whole of it gradually evaporates, the free hydrofluoric acid reacting upon the deposited silica, with formation of water; and fluoride of silicon is revived.

The most remarkable property of the fluoride of silicon is to produce, with neutral salts of potash, soda and lithia, precipitates which are gelatinous, and so transparent, as to be scarcely visible at first in the liquor, and with salts of barytes, a white and crystalline precipitate, which appears in a few seconds. Almost all the basic metallic oxides decompose this acid, when they are employed in excess; separating silica, and giving rise to metallic fluorides. When, on the other hand, no more of the base is applied than the quantity required to neutralize the free hydrofluoric acid, combinations are obtained with all bases, which are analogous to double salts; consisting of a metallic fluoride combined with fluoride of silicon, the proportion of the latter containing twice as much fluorine as the former. The formula of one of these compounds, the double fluoride of silicon and potassium, is $2\text{Si F}_3 + 3\text{K F}$, and those of other metals are similar. The ratio of 2 to 3, in the equivalents of the two fluorides which form these double salts, is unusual.

Dr. Clark, to whose judgment on the subject of atomic weights I would greatly defer, considers that the equivalent number of silicon adopted by Berzelius is too high by one third; and should be reduced from 277.31 to 184.87. With this change, silica comes to consist of 1 eq. of silicon and 2 of oxygen, or is analogous to carbonic acid; and the fluoride of silicon, of 1 of silicon and 2 of fluorine. The double fluorides, in question, may then be represented by single equivalents of fluoride of silicon and metallic fluoride; fluoride of silicon and potassium,

for instance, by $\text{Si F}_2 + \text{K F}$; and the hydrofluosilicic acid of Berzelius, by $\text{Si F}_2 + \text{H F}$. Dr. Clark connects with this an interesting speculation respecting the constitution of these salts, which he would assimilate to the ferrocyanide of potassium, considered as a compound of ferrocyanogen and potassium, $\text{Cy}_3\text{Fe} + 2\text{K}$. The fluoride of silicon and potassium may be viewed in the same way, as a compound of a salt-radical containing the silicon and all the fluorine of the salt, with potassium; that is, $\text{Si F}_3 + \text{K}$; a view which accounts for some salts of this class not being decomposed by potash, and which is favoured by the increasing number of classes of salts, which appear to be formed on a similar type.

No combination of fluorine with *oxygen* is known, nor of fluorine with *nitrogen* or *carbon*.

Fluorides of *sulphur* and of *phosphorus* were formed by Davy, by distilling the fluoride of lead or of mercury with sulphur or phosphorus, in platinum vessels. There result a sulphuret or phosphuret of the metal, and a fluoride of sulphur or of phosphorus, which volatilizes. Both of these compounds present themselves as fuming liquids. The fluoride of phosphorus is decomposed by water, hydrofluoric acid with phosphorous acid being formed; it is, therefore, a terfluoride of phosphorus, P F_3 . This fluoride is capable of taking fire and burning in air, when it is presumed that phosphoric acid is produced, and gaseous fluorine set free, which diffuses itself in the atmosphere.

CHAPTER II.

COMPOUNDS OF HYDROGEN.

SECTION I.

HYDROGEN AND SULPHUR.

SULPHURETTED HYDROGEN, or HYDROSULPHURIC ACID; *Eq.* 213.67 or 17.12; SH ; *density* 1177; $\square\square$.

Certain compounds of hydrogen with the non-metallic elements have been reserved for separate consideration, which could not be introduced with advantage at an earlier period:

namely, the compounds of hydrogen with sulphur and selenium, with nitrogen and phosphorus, and with carbon. With sulphur, hydrogen forms at least two compounds, one of which, sulphuretted hydrogen gas, is a reagent of frequent application, and considerable importance.

Preparation.—Of those metals which dissolve in dilute sulphuric acid, with the displacement of hydrogen, the protosulphurets dissolve also in the same acid, but the hydrogen then evolved carries off sulphur in combination, and appears as sulphuretted hydrogen gas. The protosulphuret of iron, which is commonly employed in this operation, is obtained by depriving yellow pyrites or bisulphuret of iron of a portion of its sulphur by ignition in a covered crucible; or formed directly by exposing to a low red heat a mixture of 4 parts of coarse sulphur and 7 of iron filings or borings in a covered stone-ware or cast iron crucible. The sulphuret of iron, thus obtained, is broken into lumps, and acted upon by diluted sulphuric acid in a gas-bottle, exactly as zinc is treated in the preparation of hydrogen gas (page 257). Sulphuretted hydrogen is evolved without the application of heat, and should be collected over water at 80 or 90°; or if collected in a gasometer or gasholder, the latter may be filled with brine, in which this gas is less soluble than in pure water. Sulphuretted hydrogen obtained by this process, generally contains free hydrogen, arising from an intermixture of metallic iron with the sulphuret. The gas may also be evolved from the action of hydrochloric acid upon the sulphuret of iron, but as it is then impregnated with the vapour of the acid, and may also, like every gas produced with effervescence, carry over drops of fluid, it should always be transmitted through water, before being applied to any purpose as pure gas. The reaction by which sulphuretted hydrogen is usually evolved, is expressed in the following equation :



Sulphuretted hydrogen, without any admixture of free hydrogen, is obtained by digesting in a flask, used as a retort, with a gentle heat, sulphuret of antimony in fine powder with concentrated hydrochloric acid, in the proportion of 1 ounce of the former to 4 ounce measures of the latter. The gas of this operation, after being passed through water and dried, may be considered as pure. It may be collected over mercury, but is gradually de-

composed by that metal, which has a strong affinity for sulphur, and hydrogen is liberated, without any change of volume. The reaction between hydrochloric acid and sulphuret of antimony may be thus expressed :



Properties.—Sulphuretted hydrogen is a colourless gas, of a strong and very disagreeable odour. Its density is 1.191.2, by the experiments of Gay-Lussac and Thenard. It consists of 2 volumes of hydrogen and 1-3rd vol. of sulphur vapour, condensed into 2 vols., which form its combining measure. By a pressure of 17 atmospheres at 50°, it is condensed into a highly limpid, colourless liquid, of sp. gr. 0.9, which is of peculiar interest as the analogue of water in the sulphur series of compounds. The solvent powers of this liquid have not been examined. The air of a chamber slightly impregnated by this gas may be respired without injury, but a small quantity of the undiluted gas inspired occasions syncope, and its respiration, in a very moderate proportion, was found by Thenard to prove fatal—birds perishing in air containing 1-1500th, and a dog, in air containing 1-800th part of this gas. Water dissolves, at 64°, 2½ volumes of this gas, and alcohol, 6 volumes. These solutions soon become milky, when exposed to air, the oxygen of which combines with the hydrogen of the gas, and precipitates the sulphur. Those mineral waters termed sulphureous, contain this gas, although rarely in a proportion exceeding 1½ per cent of their volume. They are easily recognised by their odour, and by blackening silver.

Sulphuretted hydrogen is highly combustible, and burns with a pale blue flame, producing water and sulphurous acid, and generally a deposit of sulphur when oxygen is not present in excess. A little strong nitric acid thrown into a bottle of this gas, occasions the immediate oxidation of its hydrogen, and often a slight explosion with flame, when the escape of the vapour is impeded by closing the mouth of the bottle by the finger. Sulphuretted hydrogen is immediately decomposed by chlorine, bromine and iodine, which assume its hydrogen; the odour of sulphuretted hydrogen in a room is soon destroyed, on diffusing a little chlorine through it. Tin and many other metals, heated in this gas, combine with its sulphur with flame, and liberate an equal volume of hydrogen. Potassium decomposes one moiety

of the gas in that manner, and becomes sulphuret of potassium, which unites with the other moiety without decomposition, forming a hydrosulphuret of the sulphuret of potassium. The action of other alkaline metals upon sulphuretted hydrogen is similar.

This compound has a weak acid reaction, and is generally classed with the hydrogen acids. It does not combine and form salts with basic oxides, but it unites with basic sulphurets, such as sulphuret of potassium, and forms compounds which are strictly comparable with hydrated oxides. When sulphuretted hydrogen is passed over lime at a red heat, both compounds are decomposed, and water with sulphuret of calcium is formed. The oxides of nearly all the metallic salts, whether dry or in a state of solution, are decomposed by sulphuretted hydrogen in a similar manner. But in those salts, of which the metallic sulphurets are dissolved by acids, such as salts of iron, zinc and manganese, a small quantity of a strong acid entirely prevents precipitation. These sulphurets are generally coloured, and many of them are black; hence, the effect of sulphuretted hydrogen in blackening salts of lead and silver, which renders these compounds so sensitive as tests of the presence of that substance. Sulphuretted hydrogen also tarnishes certain metals, such as gold, silver and brass, so that utensils of which these metals are the basis should not be exposed to this gas.

Persulphuret of hydrogen.—When carbonate of potash is fused with half its weight of sulphur, a sulphuret of potassium is formed containing a large excess of sulphur, which affords a solution in water of an orange red colour. The protosulphuret of potassium, with hydrochloric acid, gives sulphuretted hydrogen and chloride of potassium: H Cl and $\text{K S} = \text{H S}$ and K Cl . But when the red solution of persulphuret of potassium is poured in a small stream, into hydrochloric acid, diluted with two or three volumes of water, while chloride of potassium is formed as before, the sulphuretted hydrogen produced combines with the excess of sulphur present, and forms a yellowish oily fluid, the persulphuret of hydrogen, which falls to the bottom of the acid liquor. The result of the combination in this case appears rather capricious; for if the acid and persulphuret of potassium be mixed in the other way,—if the acid be added drop by drop to the alkaline sulphuret, then sulphuretted hydrogen gas is evolved, the whole excess of sulphur precipitates,

and no persulphuret of hydrogen is formed. The oily fluid produced by the first mode of mixing has considerable analogy in its properties to the peroxide of hydrogen, and appears, like that compound, to have a certain degree of stability imparted to it by contact with acids, while the presence of alkaline bodies on the contrary, give its elements a tendency to separate.

Thenard has observed other points of analogy between these compounds. Like peroxide of hydrogen, the persulphuret produces a white spot upon the skin. The latter compound is also resolved into sulphuretted hydrogen and sulphur by all the bodies which effect the transformation of the former into water and oxygen, such as charcoal powder, platinum, iridium, gold, peroxide of manganese, and the oxides of gold and silver, which when the persulphuret is dropt upon them, are decomposed in an instant, and even with ignition. The persulphuret of hydrogen undergoes spontaneously the same decomposition, even in well closed bottles, which are apt, on that account, to be broken. It is soluble in ether, but the solution soon deposits crystals of sulphur. Thenard finds this body not to be uniform in its composition, the proportion of sulphur often exceeding considerably 2 proportions to 1 of hydrogen. The oily fluid may, therefore, be sometimes one and sometimes another compound of sulphur and hydrogen.*

SECTION II.

HYDROGEN AND SELENIUM.

Seleniuretted hydrogen, H Se .—One compound of these elements is known, which is obtained by processes similar to those already described, and possesses considerable analogy to sulphuretted hydrogen. It is a colourless gas, soluble in water, and readily decomposed by the conjoint action of water and air, with precipitation of selenium. All metallic solutions, even those of zinc and iron, when neutral, are precipitated by solution of seleniuretted hydrogen, and the metallic seleniurets are generally black or dark brown, with the exception of those of zinc, manganese and cerium, which have a flesh colour. The odour of this gas is exactly similar to that of sulphuretted hydrogen, but it was found, by Berzelius, to exercise so violent an action

* An. de Ch. et de Ph. t. 48, p. 79.

upon the respiratory organs, as to make the inspiration of it, even in a highly diluted state, a most painful and even dangerous experiment (*Traité*, I. 340).

SECTION III.

HYDROGEN AND NITROGEN.

AMIDOGEN.

Eq. 202 or 16.9 ; N H_2 or Ad ; not isolable.

Hydrogen and nitrogen do not combine directly, but three compounds of these elements are generally admitted to exist, only one of which, however, ammonia, can be obtained in a separate state. It is even highly probable that amidogen is the only direct combination of these elements, and that the other two are compounds of amidogen with hydrogen. These compounds are—

Amidogen . .	N H_2	N H_2
Ammonia . .	$\text{N H}_2 + \text{H}$	N H_3
Ammonium . .	$\text{N H}_2 + 2\text{H}$	N H_4

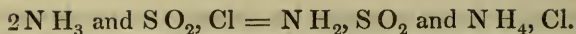
Judging from the nature of the combinations in which amidogen is found, it appears to be a compound of the salt-radical class, in which it occupies a low place, superior to oxygen, but considerably inferior to chlorine, or perhaps even sulphur. The *white precipitate* of pharmacy, formed on adding ammonia to a solution of chloride of mercury, is a body in which amidogen was proved to exist by the analysis of Dr. Kane, which has been repeated and confirmed by Ullgren. The term *amide* being applied to combinations of amidogen, and the symbol Ad assigned to it, white precipitate is a compound of chloride of mercury with amide of mercury, and is expressed by $\text{Hg Cl} + \text{Hg Ad}$. Dr. Kane has also shown that the black compound obtained on washing calomel or subchloride of mercury with ammonia, is a corresponding combination of subchloride with subamide of mercury, $\text{Hg}_2\text{Cl} + \text{Hg}_2\text{Ad}$; and he has ascertained the existence of amidogen in a variety of other mercurial compounds. But it is to be observed of the metallic combinations of amidogen, that those which have been certainly established are confined to that metal, and also that amides of mercury have never been

obtained in a separate state, but always in combination with another mercurial salt. The idea was thrown out by Dumas, that the explosive compounds of nitrogen might contain amidogen, and the same view has been applied to the fulminating compounds produced by the action of ammonia upon the oxides of silver and gold; but these views have not yet been fully verified by analysis.

Potassium, heated in ammoniacal gas, N H_3 , disengages hydrogen, as when it acts upon water. If ammonia were then simply reduced to the state of amidogen, 4 volumes of the former should be decomposed to evolve 2 volumes of hydrogen; but in the numerous experiments of Gay-Lussac and Thenard, never more than $3\frac{1}{2}$ volumes of ammonia were required to furnish 2 volumes of hydrogen, and consequently a small portion of the hydrogen must be furnished by the decomposition of amidogen itself. The compound of potassium, which is a fusible solid matter of an olive-green colour, likewise contains undecomposed ammonia. The basis of it is, probably, a compound of potassium and amidogen, but its constitution is very problematical. Ever since the formation of this compound, by Davy and the chemists named above, the existence of such a body as amidogen has been a floating speculation among chemists. But it was first fixed and distinctly enunciated by Dumas, in his theory of the amides, in reference to a class of compounds of which he is the discoverer.

Oxamide, $\text{N H}_2\text{C}_2\text{O}_2$.—When oxalate of ammonia is decomposed by heat, a white insoluble sublimate is obtained, which was termed oxamide by Dumas, and viewed as a combination of amidogen and carbonic oxide, $\text{N H}_2\text{C}_2\text{O}_2$; being formed by the abstraction of the elements of two atoms of water from oxalate of ammonia, of which the formula is $\text{N H}_4\text{O}, \text{C}_2\text{O}_3$. When oxamide is boiled with an alkali or with an acid, the two atoms of water are again assumed, and oxalic acid with ammonia reproduced. Similar amides may be formed from other organic acids.

Sulphamide, $\text{N H}_2, \text{S O}_2$.—This is a compound exactly analogous to oxamide, containing the radical sulphurous acid, S O_2 , instead of C_2O_2 , in combination with amidogen. Sulphamide was formed, by Regnault, by the action of dry ammonia upon chlorosulphuric acid, when 2 equivalents of ammonia and 1 of chlorosulphuric acid become sulphamide and hydrochlorate of ammonia :



M. Regnault did not succeed completely in separating sulphamide from the hydrochlorate of ammonia; these bodies are nearly equally soluble, both in water and alcohol, and separate very imperfectly by crystallization. Sulphamide has a great attraction for moisture, and quickly deliquesces in the air, in which respect it differs completely from the product $\text{N H}_3, \text{S O}_3$, resulting from the combination of anhydrous sulphuric acid with dry ammoniacal gas, and which some chemists have viewed as a hydrated sulphamide, $\text{N H}_2, \text{S O}_2 + \text{H O}$. The solution of sulphamide, in water, does not undergo any spontaneous change; a solution even acidulated with hydrochloric acid and mixed with chloride of barium, in a close vessel, was not sensibly disturbed by the formation of sulphate of barytes in the course of a month. But at the boiling point, sulphamide changes slowly into the ordinary sulphate of ammonia by the fixation of the elements of water; and the presence of a strong acid facilitates that transformation.

Carbamide, $\text{N H}_2, \text{C O}$.—Chlorocarbonic gas (page 378) condenses ammoniacal gas, forming a compound which has hitherto been viewed as a chlorocarbonate of ammonia, $2\text{N H}_3 + \text{C O}, \text{Cl}$, but which M. Regnault finds to be a mixture of carbamide and hydrochlorate of ammonia, $\text{N H}_2, \text{C O}$ and $\text{N H}_4, \text{Cl}$. This compound is not deliquescent, dissolves easily in water and in alcohol slightly diluted. Carbamide is not decomposed by acetic or oxalic acid, nor by the strongest acids if diluted, but concentrated nitric acid occasions the evolution of carbonic acid. Its solution is not disturbed by chloride of barium. The elements of urea, $\text{N}_2\text{H}_4, \text{C}_2\text{O}_2$, are the same as those of carbamide, but the equivalent of the former, inferred from its capacity of saturation as an organic base, is double that of the latter.*

AMMONIA.

Eq. 214.48 or 17.19; N H_3 or H Ad ; density 591.5;

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Ammonia is a volatile alkali, which derives its name from sal ammoniac, a salt from which it is generally extracted, and which received its title from being first prepared in the district of

* Regnault, *An. de Ch. et de Ph.* t. 69, p. 180.

Ammonia, in Libya. It is produced in the destructive distillation of all organic matters containing nitrogen, which has given rise to one of its popular names, the spirits of hartshorn. It is also produced during the putrefaction of the same matters in the atmosphere. In the mineral kingdom, it appears often to be formed in oxidation, when effected by the simultaneous action of air and water, as in the rusting of iron, and a trace of it is always found in the native oxides of iron, in the varieties of clay, and in some other minerals.

Preparation.—In a state of purity, ammonia is a gas, of which the *liquor* or *aqua ammoniæ* is a solution in water. This solution, which is of constant use as a reagent, is prepared by mixing intimately sal ammoniac (hydrochlorate of ammonia) with an equal weight of slaked lime, and distilling the mixture in a glass retort, by the diffused heat of a chauffer or sand-pot. Ammoniacal gas comes off, which should be passed through a small quantity of water, to arrest a little dust of lime that is carried along with it, and afterwards be conducted into a quantity of distilled water, to condense it, equal to the weight of the salt employed. Chloride of calcium and the excess of lime remain in the retort, and a considerable quantity of water is liberated in the process, and distils over with the ammonia. This important reaction is explained in the following diagram :

PROCESS FOR AMMONIA.

Before decomposition.		After decomposition.	
669 Hydrochlorate of ammonia	{	Ammonia 214½	— 214½ Ammonia.
	{	Hydrogen 12½	
	{	Chlorine 442	
356 Lime . . .	{	Oxygen . 100	— 112½ Water.
	{	Calcium . 256	— 698 Chloride of calcium.
1025		1025	1025

Or in symbols : $\text{N H}_4, \text{Cl}$ and $\text{Ca O} = \text{N H}_3$ and H O and Ca Cl .

To obtain ammoniacal gas, the solution prepared by the preceding process may be boiled by a gentle heat, when the gas is first expelled from its superior volatility; or the gas may be derived at once from sal ammoniac, mixed with twice its weight of quicklime in a small retort, and collected over mercury.

Properties.—Ammonia is a colourless gas, of a strong and

pungent odour, familiar in spirits of hartshorn. It is composed of 2 volumes of nitrogen and 6 of hydrogen, condensed into 4 vols., which form the combining measure of this gas. Ammonia is resolved into its constituent gases, in these proportions, when transmitted through an ignited porcelain tube containing iron or copper wire, while the metal, at the same time, becomes brittle, and is supposed by Despretz to absorb nitrogen, although this is doubtful. By a pressure of 6.5 atmospheres, at 50°, it is condensed into a transparent colourless liquid, of which the sp. gr. is about 0.76. Ammoniacal gas is inflammable in air in a low degree, burning in contact with the flame of a taper. A mixture of this gas with an equal volume of nitrous oxide may be detonated by the electric spark, and affords water and nitrogen. Water is capable of dissolving several hundred times its volume of ammoniacal gas, and the solution is always specifically lighter, and has a lower boiling point than pure water. According to the observations of Davy, solutions of sp. gr. 0.872, 0.9054 and 0.9692 contain respectively 32.5, 25.37 and 9.5 per cent of ammonia. Ammoniacal gas is also largely soluble in alcohol.

Solution of ammonia has an acrid alkaline taste, and produces blisters on the tongue and skin. When cooled slowly to -40° , it crystallizes in long needles of a silky lustre. The solution has a temporary action upon turmeric paper, which it causes to be brown while humid; it also restores the blue colour of litmus reddened by an acid, changes the blue colour of the infusion of red cabbage into green, and neutralizes the strongest acids, properties which it possesses in common with the fixed alkalies. When ammonia is free, it may always be detected by its odour, by forming dense, white fumes with hydrochloric acid, and by forming a deep blue solution with salts of copper.

Ammonia, in solution, is decomposed by chlorine, with the evolution of nitrogen gas and formation of hydrochlorate of ammonia; when ammonia and chlorine, both in the state of gas, are mixed together, the action that ensues is attended with flame. Dry iodine absorbs ammoniacal gas, and forms a brown viscous liquid (page 388), which water decomposes, dissolving out hydriodate of ammonia, and leaving a black powder, which is the explosive iodide of nitrogen.

The consideration of ammonia, as a compound of amidogen and hydrogen, was involved in the explanation given by Dumas

of the formation of oxamide and other amides ; but ammonia was first fully studied under this point of view by Dr. Kane, in his elaborate and valuable paper on the compounds of ammonia lately published.* He has there successfully illustrated the nature of the two following classes of ammoniacal compounds, namely, those of ammonia with dry acids, and with anhydrous salts.

Ammonia and anhydrous oxygen acids.—Ammoniacal gas is condensed by dry carbonic acid gas, sulphurous acid, anhydrous sulphuric acid, &c., and saline compounds are formed which are not to be confounded with the ordinary salts of ammonia, these containing ammonium. The class of salts in question has been minutely studied by Rose.† Ammonia, or the amide of hydrogen being viewed by Dr. Kane as a weak base, like water or the oxide of hydrogen, these salts are compared by him with hydrated acids or salts of water. They are the true salts of ammonia as a base.

With carbonic acid ammonia combines only in the proportion of single equivalents, or 4 vols. of ammoniacal gas with 2 vols. of carbonic acid. This carbonate of ammonia is a light, white, very volatile powder, of a strong ammoniacal odour, in the vapour of which the constituent gases are united without condensation. The density of this vapour is, therefore, 902. This compound exists in, and is the cause of the strong odour of the smelling salts, or carbonate of ammonia of the shops. By water it is decomposed, and resolved into free ammonia and the bicarbonate of the oxide of ammonium.

With sulphurous acid gas, ammonia condenses in two proportions : namely, 4 vols. of ammonia with 2 and 4 vols. of sulphurous acid, forming a neutral sulphite and a bisulphite of ammonia. The neutral salt attaches itself to the sides of the vessel in which the gases are mixed as a solid crust, or in feathery crystals of a reddish yellow colour. It rapidly absorbs moisture from the air, becomes white, and changes into the neutral sulphite of the oxide of ammonium.

With anhydrous sulphuric acid, ammonia appears also to

* Transactions of the Royal Irish Academy, vol. 19, pt. I.

† On the Combinations of Ammonia with Carbonic Acid ; Taylor's Scientific Memoirs, vol. 2, p. 98 :

Sur le Sulfate anhydre d'Ammoniaque, An. de Ch. et de Ph. t. 62, p. 389.

Sur le Sulfite anhydre d'Ammoniaque, *Ib.* p. 407.

form two combinations, only one of which, however, the neutral sulphate of ammonia, has been obtained in a definite state. This salt appears to dissolve in water without decomposition, and neither of its constituents is immediately affected or fully precipitated by the reagents which usually have that effect. Thus chloride of strontium and chloride of calcium do not disturb its solution for several hours; chloride of platinum precipitates, at first, only a small portion of the ammonia, and chloride of barium, a small portion of the sulphuric acid of the salt. By boiling, its solution is gradually, but never completely converted into the ordinary sulphate of the oxide of ammonium, and this conversion seems always to precede the action of the reagents mentioned upon it. But, as Dr. Kane remarks, this sulphate of ammonia contains, on the binary theory of salts, a peculiar salt-radical, SO_3, NH_2 , and not SO_4 united with H; so that its salt-radical is not necessarily precipitated in the same circumstances as the salt-radical of a sulphate.

Ammonia with anhydrous salts.—Ammoniacal gas is absorbed by many anhydrous salts, and easily expelled from several of them again by heat. These combinations have also been most fully examined by Rose.* In many of them, the ammonia appears to discharge a function analogous to that of water of crystallization in salts, a function which is in accordance with its constitution as an amide of hydrogen. The salt generally rises in temperature during the absorption of the gas, and forms a bulky light powder. Sulphate of manganese absorbs 2 equivalents of ammonia, sulphate of zinc $2\frac{1}{2}$, sulphate of copper $2\frac{1}{2}$, sulphate of nickel 3 equivalents, sulphate of cobalt and sulphate of cadmium also 3, sulphate of silver 1 equivalent, nitrate of silver absorbs 3 equivalents, chloride of calcium and chloride of strontium absorb 4 equivalents, chloride of copper 3, chloride of cobalt 2, chloride of lead $\frac{3}{4}$ ths of an equivalent, chloride of silver $1\frac{1}{2}$, subchloride of mercury and chloride of mercury $\frac{1}{2}$ eq., iodide of mercury 1 eq. In some of these salts, the ammonia is more intimately combined than in others; the compound of chloride of mercury with ammonia, for instance, may be sublimed without decomposition, while the compound with iodide of mercury loses all its ammonia by exposure to the air; and in some salts, one portion of ammonia is retained more strongly than the rest; this I found to be the case with half an equiva-

* An. de Ch. et de Ph. t. 62, p. 308.

lent in several of the sulphates, and with a whole equivalent in several of the chlorides of the magnesian family.

Ammoniated salts, closely related to the preceding, are often obtained on transmitting ammoniacal gas through a strong solution of such salts as, in the dry state, combine with ammonia. Nitrate of silver crystallizes with two atoms of ammonia (G. Mitscherlich); nitrate of copper, with two also, and no water (Kane); sulphate of copper, with two ammonia and one water; chlorides of copper and zinc, with the same (Kane).

AMMONIUM.

Eq. 226.96 or 18.19; NH_4 or H_2Ad ; not isolable.

A compound radical consisting of ammonia with an additional atom of hydrogen, was first supposed to exist in the ordinary salts of ammonia by Berzelius, and termed ammonium. This body has never been insulated, but is supposed to appear, in a certain experiment, in combination with mercury, and possessed of the metallic character (page 176). It is not necessary, however, that ammonium be a metal to be admitted as a basyle, and its existence is now generally rested upon evidence of a different nature. The compounds of ammonium are always strictly isomorphous with the corresponding compounds of potassium.

Chloride of ammonium, hydrochlorate or muriate of ammonia, sal ammoniac, NH_4, Cl .—This salt is formed when ammonia is neutralized by hydrochloric acid; NH_3 and $HCl = NH_4, Cl$. It is prepared in large quantity from the ammoniacal liquor obtained in the distillation of bones, in the manufacture of animal charcoal, and from the liquor which condenses in the distillation of coal for gas. These liquors contain ammonia principally in the state of carbonate and hydrosulphuret, which may be converted into chloride of ammonium by the addition of hydrochloric acid. The salt is purified by crystallization, and sublimed in vessels of iron or earthenware, in the upper part of which it condenses and forms a solid cake, the condition in which sal ammoniac is always met with in commerce.

Sal ammoniac is tenacious and difficult to reduce to powder; its sp. gr. is 1.45. It has a sharp and acrid taste, and dissolves in 2.72 parts of cold, and in an equal weight of boiling water; it

is also soluble in alcohol. It generally crystallizes from solution in feathery crystals, which are formed of rows of minute octohedrons attached by their extremities.

A corresponding bromide, iodide and fluoride of ammonium may be formed by neutralizing ammonia with hydrobromic, hydriodic and hydrofluoric acids.

Sulphurets of ammonium.—When 4 volumes of ammonia combine with 2 of sulphuretted hydrogen, the sulphuret of ammonium is produced; N H_3 and $\text{H S} = \text{N H}_4, \text{S}$. Ammonium combines with sulphur in several other proportions, which are obtained on mixing and distilling the various degrees of sulphuration of potassium with sal ammoniac. In the reciprocal decomposition which occurs, the potassium combines simply with chlorine, and the ammonium with sulphur. The following compounds are generally enumerated: $\text{N H}_4, \text{S}$; $\text{N H}_4, \text{S} + \text{H S}$; $\text{N H}_4, \text{S}_3$ and $\text{N H}_4, \text{S}_5$. The protosulphuret has long been formed by distilling a mixture of quicklime, sulphur and sal ammoniac, and known under the name of the *fuming liquor of Boyle*. It is a volatile liquid, the vapour of which is decomposed by oxygen, and thus fumes produced. The second compound, which is a hydrosulphuret of the sulphuret of ammonium, is formed by transmitting sulphuretted hydrogen through solution of ammonia to saturation. This liquid is generally called the hydrosulphuret of ammonia, and is the form in which sulphuretted hydrogen is most frequently used as a reagent. All the sulphurets of ammonium are soluble in water and alcohol without decomposition.

Nitrate of ammonium, $\text{N H}_4 \text{O}, \text{N O}_5$.—When nitric acid is saturated with ammonia, a salt is obtained which crystallizes in six-sided prisms, and is isomorphous with nitrate of potash. Besides the elements of nitric acid and ammonia, this salt contains an atom of water which cannot be separated from it, which is also found in, and is equally essential to the salts formed by neutralizing all other oxygen acids by ammonia, such as sulphurous acid, sulphuric, carbonic, &c., in contact with water. The hydrogen of this water is assigned to the ammonia, to form ammonium, which the oxygen converts into oxide of ammonium; so that the product is nitrate of the oxide of ammonium; or N H_3 and $\text{H O}, \text{N O}_5 = \text{N H}_4 \text{O}, \text{N O}_5$. This salt deflagrates with flame, when thrown upon red hot coals. When decomposed between 3 and 400°, it is resolved into water and nitrous oxide (page 283).

Carbonates of ammonium.—The neutral carbonate of oxide of ammonium appears not to exist in a free state, but by distilling the sesquicarbonate of ammonia of the shops, by a gentle heat. Rose obtained a volatile crystalline salt, which may be viewed as a compound of carbonate of ammonia with carbonate of ammonium : $\text{N H}_3, \text{C O}_2 + \text{N H}_4 \text{O}, \text{C O}_2$. When the commercial salt is exposed to the air, it loses its pungent odour, and a white friable mass remains, which is the bicarbonate of ammonium, or carbonate of water and oxide of ammonium : $\text{H O}, \text{C O}_2 + \text{N H}_4 \text{O}, \text{C O}_2$. This is a stable salt, and may be dissolved and crystallized without change.

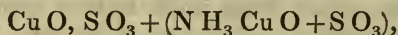
The sesquicarbonate of ammonia of the shops is a crystalline transparent mass, which Rose finds to have generally, but not always, the composition assigned to it by Mr. Phillips, or to contain 3C O_2 with 2N H_3 and 2H O . Rose is disposed to consider it a compound of carbonate of ammonia and bicarbonate of oxide of ammonium, or $\text{N H}_3 \text{C O}_2 + (\text{H O}, \text{C O}_2 + \text{N H}_4 \text{O}, \text{C O}_2)$. Mr. Scanlan has shown that a small quantity of water dissolves out the carbonate from this salt, and leaves the bicarbonate, which is the least soluble. This observation does not prove the commercial salt to be a mechanical mixture of the two salts derived from it, as many undoubted compounds of two salts are decomposed by water, when one of the constituent salts is much more soluble than the other. Another salt was obtained by Rose, in well formed crystals, of which the ammonia and carbonic acid are in the proportions of the sesquicarbonate, but with three additional atoms of water. No less than twelve different carbonates of ammonia are described by that chemist, (*Scientific Memoirs*, ii, 98).

Sulphate of ammonium, $\text{N H}_4 \text{O}, \text{S O}_3 + \text{H O}$.—This is a highly soluble salt, which possesses an atom of water of crystallization, in addition to the atom which is essential to its constitution. The salt may be deprived of the former by a gentle heat.

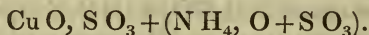
It is to be observed that salts of this class are still generally named as salts of ammonia, although admitted to contain ammonium.

Compounds of ammonia and metallic salts, supposed to resemble the ammonium compounds.—The whole or a portion of the ammonia absorbed by certain anhydrous salts is retained with great force, and cannot be separated from them by heat. Anhydrous chloride of copper, for instance, absorbs a single equi-

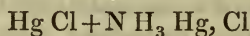
valent of ammonia with the greatest avidity, and forms a green fusible matter, which the close analogy between copper and hydrogen would lead us to view as analogous in constitution to the compound formed by chloride of hydrogen and ammonia, or chloride of ammonium. It will, therefore, be represented as composed of chlorine united with ammonium, containing an atom of copper, in place of the fourth atom of hydrogen, or as $\text{N H}_3 \text{ Cu, Cl}$, which may be called chloride of cuprammonium. The sulphate of copper, in like manner, retains half an equivalent of ammonia with great force, and forms a compound which may be represented as sulphate of copper combined with sulphate of cuprammonium :



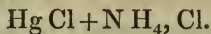
which is analogous to the double sulphate of copper and ammonium :



Chloride of mercury forms a similar compound with half an equivalent of ammonia :



analogous to sal alembroth, or the compound of chloride of mercury and sal ammoniac :



A different view of these and the other ammonium compounds is advocated by Dr. Kane. Sal ammoniac is considered by him as a species of double salt, as amide of hydrogen with chloride of hydrogen, $\text{H Ad} + \text{H Cl}$; and the salt I have named, chloride of cuprammonium, as a corresponding amide of hydrogen with chloride of copper, $\text{H Ad} + \text{Cu Cl}$. We agree in supposing these two salts to have the same constitution, but differ as to what that constitution is. To adapt the same explanation to the oxygen acid compounds, such as sulphate of ammonium, Dr. Kane assimilates them to the salts of the magnesian class, which contain two equivalents of oxide. Adopting the hypothesis that two atoms of that class (in which water is included) are equivalent in combination to one of the potash class, he views sulphate of copper, possessing what I term its atom of constitutional water, as a compound of sul-

phuric acid with a base, which consists of an atom of oxide of copper and an atom of water, and represents it thus :

Sulphate of copper . . $\text{Cu O, H O} + \text{S O}_3$;

to which he assimilates the

Sulphate of ammonium . $\text{Ad H, H O} + \text{S O}_3$.

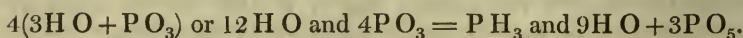
The hypothesis of the equivalency of two atoms of the magnesian and one of the potash class, has received new support from Dr. Kane's researches; but it is still (in my opinion) too doubtful to form a safe basis for any theoretical superstructure. At the same time, this hypothesis has enabled Dr. Kane to develop many new and interesting relations among the ammoniacal compounds, and may, perhaps, present a closer and more distinct view of the intimate constitution of these bodies, than the ammonium theory exhibits. At present, however, our theories of the constitution of compounds are too uncertain to be regarded otherwise than as artificial aids to facilitate our conception of the manner in which the formation of these bodies occurs, and of the transformations which they undergo; and a theory of constitution is, therefore, adopted more for its convenience than its truth. This state of things leads to the retention of the ammonium theory, which has introduced a degree of simplicity into our views of that particular class of ammoniacal compounds to which it is applicable, that could not easily be exceeded. But its adoption must not be allowed to preclude the consideration of other theories, such as that of Dr. Kane, which facilitate investigations in the meantime, and may prove to be truer to nature in the end.

SECTION IV.

HYDROGEN AND PHOSPHORUS.

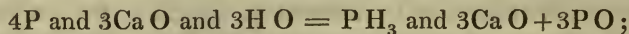
Solid hydruret of phosphorus.—Magnus forms a phosphuret of potassium, by fusing phosphorus and potassium under naphtha. When this compound is thrown into water, a compound of phosphorus and hydrogen precipitates in the form of a yellow powder. It contains less hydrogen than the following compound.

Phosphuretted hydrogen gas, PH_3 .—This gas, which is remarkable for its occasional spontaneous inflammability in air, was discovered by Gengembre in 1783, and has been successively investigated by several chemists; but its true nature was first ascertained by Rose, who proved it to be a compound analogous in constitution to ammoniacal gas, having phosphorus in the place of nitrogen. The pure gas is obtained by heating hydrated phosphorous acid, which is resolved into phosphuretted hydrogen and hydrated phosphoric acid; thus,



This gas does not inflame spontaneously when allowed to escape into air, but kindles when a light is applied to it, and burns with the white flame of phosphorus. A little air added to the gas, which had no effect at first, has been observed to produce occasionally an explosion after a time. The gas consists of 1 volume of phosphorus vapour and 6 volumes of hydrogen, condensed into 4 volumes, so that it has the same combining measure as ammoniacal gas. Its density is 1185. Phosphuretted hydrogen has a disagreeable alliaceous odour, is but slightly soluble in water, and has no alkaline reaction.

The same gas, in a self-inflammable state, is obtained by boiling phosphorus, lime and water together. The first effect is the formation of hypophosphite of lime, with the evolution of phosphuretted hydrogen gas :



and phosphuretted hydrogen is again evolved, but mixed with a considerable quantity of free hydrogen, when the hydrated hypophosphite of lime is evaporated to dryness, phosphate of lime being the residuary product. The self-inflammability of this gas must depend upon something extraneous. Rose has shown that the gas, after being passed through a long tube containing chloride of calcium, to dry it thoroughly, retains this property, for days, and undergoes no change in composition, whether kept in obscurity or exposed to sunshine,* and, therefore, rejects the theory of M. Leverrier,† that the property in question is

* Liebig's *Annalen der Pharmacie*, v. 30, p. 320. (1839.)

† *An. de Ch. et de Ph.* t. 60, p. 174.

due to another gaseous compound of phosphorus and hydrogen, $P + 2H$, present in small quantity, and supposed to be decomposed by light, and to deposit a solid hydruret $P + H$, while the gas ceases to be self-inflammable. It was observed by myself,* that the presence of phosphorus vapour does not communicate spontaneous inflammability to the gas prepared from phosphorous acid; that the gas from hydrate of lime and phosphorus is deprived of this property by porous absorbents, such as charcoal, by phosphoric acid, and by a most minute quantity of several combustible bodies, such as potassium, the vapours of ether and essential oils; and that the property was communicated to the gas of either process, by the addition of a most minute quantity of the vapour of peroxide of nitrogen or of nitrous acid, varying from 1-1000th to 1-10,000th of the volume of the gas. The hydrogen gas which first comes off on making an addition of sulphuric acid to the gas bottle with zinc (page 257), sometimes contains enough of peroxide of nitrogen, to impart spontaneous inflammability to phosphuretted hydrogen, to which it may be added. The self-inflammable gas from phosphorus and hydrate of lime cannot contain peroxide of nitrogen, but it might be imagined to possess a trace of a corresponding compound of phosphorus and oxygen, if such a compound exists.

Phosphuretted hydrogen decomposes some metallic solutions, such as those of copper and mercury, and forms metallic phosphurets. When the gas is pure, it is entirely absorbed by sulphate of copper and by chloride of lime. With hydriodic acid, phosphuretted hydrogen forms a crystalline compound, which is interesting from its analogy to sal ammoniac. It may be formed by mixing together its constituent gases over mercury; or more easily by introducing into a small tubulated retort, a mixture of 60 parts of iodine, 15 of phosphorus finely granulated, and mixing these bodies intimately with pounded glass; 8 or 9 parts of water are then added to the mixture, and the vapours which immediately come off are allowed to escape by a glass tube open at both ends, adapted to the beak of the retort, in which beautiful small crystals of the salt condense, of a diamond lustre. Rose has lately observed that these crystals, contrary to what is generally supposed, do not belong to the regular system, and

* Phil. Mag. 3rd Series, vol. 5, p. 401.

are, therefore, not isomorphous with sal ammoniac. They are decomposed by water, with evolution of phosphuretted hydrogen.

Phosphuretted hydrogen, like ammonia, combines with the perchlorides of tin, titanium, chromium, iron, and antimony, forming white saline bodies. The combination with bichloride of tin is decomposed, with escape of the gas in the non-inflammable state, by water, and in the self-inflammable condition by solution of ammonia.

CHAPTER III.

COMPOUNDS OF CARBON.

SECTION I.

CARBON AND HYDROGEN.

Light carburetted hydrogen, CH_2 .—This gas is a constant product of the putrefactive decomposition of wood and other compounds of carbon, under water, and is most readily obtained by stirring the mud at the bottom of stagnant pools, and collecting the gas as it rises in an inverted bottle and funnel. It always contains 10 or 20 per cent of carbonic acid, which may be separated from it by lime-water, and a small proportion of nitrogen. Carburetted hydrogen also issues, in some places, in considerable quantities from fissures in the earth, coming often from subterraneous deposits of coal; and in the working of coal mines, it is found pent up in cavities, and would appear sometimes to be discharged from the fresh surface of the coal in sensible quantity. Hence, this gas is sometimes described as the inflammable air of marshes, and the fire-damp of mines. It is the most considerable constituent of coal gas, and of the gaseous mixture obtained on passing the vapour of alcohol through an ignited porcelain tube, but no artificial process is known to afford this gas in a state of purity.

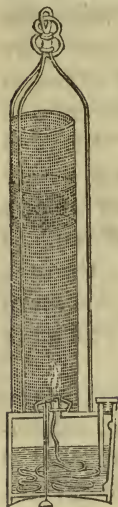
The density of light carburetted hydrogen is 559.5, and 1 volume of it contains 1 vol. of carbon vapour, and 2 vols. of

hydrogen; but the combining measure and equivalent of this compound are unknown. It is inodorous, neutral, respirable when mixed with air, not more soluble in water than pure hydrogen, and has never been liquefied. Carburetted hydrogen requires twice its bulk of oxygen to burn it completely, and affords water and an equal bulk of carbonic acid. In air it burns, when lighted, with a strong yellow flame. It is a compound of considerable stability, but is decomposed in part when sent through a tube heated to whiteness, and resolved into carbon and hydrogen. This gas is not affected in the dark by chlorine, but when the mixture of these gases, in a moist state, is exposed to light, carbonic and hydrochloric acid gases are produced.

Although instantly kindled by flame, carburetted hydrogen requires a high temperature to ignite it. Hydrogen, sulphuretted hydrogen, and olefiant gas are all ignited by a glass rod heated to low redness, but glass must be heated to bright redness or to whiteness, to inflame carburetted hydrogen. Sir H. Davy discovered that flame could not be communicated to an explosive mixture of carburetted hydrogen and air, through a narrow tube, because the cooling influence of the sides of the tube prevented the gaseous mixture contained in it from ever rising to the high temperature of ignition. A metallic tube has a greater cooling property, from its high conducting power, and consequently obstructs to a greater degree the passage of flame, than a similar tube of glass; and even the meshes of metallic wire-gauze, when they did not exceed a certain magnitude, were found to be impermeable by flame. Experiments of this kind may be made upon coal-gas, the flame of which will be found incapable of passing through a sheet of iron-wire trellis, containing not less than 400 holes in the square inch. If the gas be allowed to pass through the trellis, and kindled above it, the flame, it will be found, does not return through the apertures to the jet whence the gas issues. Upon these observations, Sir H. Davy founded his invaluable invention of the safety lamp, an instrument indispensable to the safe working of the most extensive and valuable of our coal fields.

The safety lamp, as left by Davy, is simply an oil lamp, inclosed in a cage of wire-gauze, the upper part of which is double, (Fig. 43.) Mr. Buddle uses iron-wire gauze for the lamp,

FIG. 43.



containing from 784 to 800 holes in the square inch. A crooked wire, which works tightly in a narrow tube passing upwards through the body of the lamp, affords the means of trimming the wick, without undoing the wire-gauze cover of the lamp. When the lamp is carried into an atmosphere charged with fire-damp, a blue flame is observed within the gauze cylinder, from the combustion of the gas, and the flame in the centre of the lamp may be extinguished. The miner should then withdraw, for although the gauze has often been observed to become red-hot, without inflaming the external explosive atmosphere, yet the texture of the gauze may be destroyed, if retained long at so high a temperature. It has always been known, since this lamp was first proposed, that when it is exposed to a strong current of the explosive mixture, the flame may pass too quickly through the apertures of the gauze to be cooled below the point of ignition, and, therefore, communicate with the external atmosphere. But this is easily prevented by protecting the lamp from the draught, and an accident from this cause is not likely to occur in a coal mine.*

Carburetted hydrogen does not explode when mixed with air in a proportion much above or below the quantity necessary for its complete combustion. With 3 or 4 times its volume of air it does not explode at all, with $5\frac{1}{2}$ or 6 volumes of air it detonates feebly, and with 7 to 8 most powerfully. With 14 volumes of air, the mixture is still explosive, but with larger proportions of air, the gas only burns about the flame of the taper. The large quantity of air which is then mixed with the gas, absorbs so much heat as to prevent the temperature of the gaseous atmosphere from rising to the point of ignition.

Coal gas.—The products of the distillation of coal in an iron retort are of three kinds : a black oily liquid, of a heterogeneous nature, known as coal-tar, of which a considerable constituent, according to M. Dumas, is benzin; a watery fluid,

* For additional information respecting the safety lamp, the reader is referred to Davy's Essay on Flame, to Dr. Paris's Life and Dr. J. Davy's Life of Sir H. Davy, and to the Report of the Parliamentary Committee on accidents in mines, 1835.

known as the ammoniacal liquor, and the elastic fluids which form coal gas. To purify the gas, it is cooled by transmitting it through iron tubes or shallow boxes, in which it deposits some condensible matter; and it is afterwards exposed to milk of lime, to absorb sulphuretted hydrogen, which it invariably contains, and frequently afterwards to solution of sulphate of iron, which arrests a little hydrosulphuret of ammonia and a trace of hydrocyanic acid. The hydrate of lime is sometimes applied in the state of a damp powder, and not diffused through water.

Dr. Henry obtained the following results from an examination of the gas from the best cannel coal, at different periods of the distillation :

COAL GAS IN 100 VOLUMES.

	Density.	Olefant gas.	Carburetted hydrogen.	Carbonic oxide.	Hydrogen.	Nitrogen.
At beginning of process. . .	650	13	82.5	3.2	0	1.3
After five hours	500	7	56	11	21.3	4.7
After ten hours	345	0	20	10	60	10

Besides the constituents mentioned, coal gas when first made, contains small quantities of

Ammonia,	Hydrocyanic acid,
Sulphuretted hydrogen,	Sulphuret of carbon,
Carbonic acid,	Naphtha vapour.*

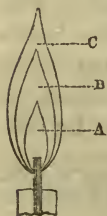
All of these bodies are separated from it in the process of purification, except the two last, namely, naphtha vapour, which is the chief cause of the odour of coal gas, and sulphuret of carbon, which affords a little sulphurous acid when the gas is burned. The heterogenous nature of the gaseous mixture is well shown upon introducing a quantity of dry iodine into a bottle of it, when several liquid and solid compounds of iodine are formed with the different hydrocarburets present. Iodine, on the other hand, is not affected in the slightest degree by fire-

* Dr. Henry's papers on coal gas are contained in the Phil. Trans. for 1808, 1820, and 1824; his instructions for the analysis of mixed gases, in his Elements of Experimental Chemistry (1829), vol. 2, p. 517.

damp, but remains with its metallic lustre unchanged in that gas. Indeed, in the ordinary fire damp no other combustible gas whatever can be found, besides light carburetted hydrogen.

The superiority of coal gas, in illuminating power, depends principally upon the high proportion of olefiant gas and the denser hydrocarburets which it contains. The free hydrogen and carbonic oxide present give no light, and are positively injurious. As the highly illuminating constituents are dense, and contain much carbon, the value of coal gas is to a certain extent proportional to its density, and to the quantity of oxygen which it requires for complete combustion. In the analysis of coal gas, the different gases may thus be separated: 1st. Olefiant gas, naphtha vapour, and similar hydrocarburets, by mixing the gas, in a dark place, with half its bulk of chlorine, and afterwards washing with caustic potash; 2ndly, carbonic oxide by potassium gently heated in the gas; 3rdly, the proportion of light carburetted hydrogen may be determined by detonating the mixture in a eudiometer (page 278), with a measured quantity of oxygen, and ascertaining the quantity of carbonic acid formed, which retains the volume of the carburetted hydrogen; 4thly, the free hydrogen, by observing the quantity of oxygen remaining, by means of a stick of phosphorus introduced into the gas, and thereby ascertaining the quantity of oxygen consumed in the combustion; from this quantity deduct twice the measure of the carburetted hydrogen, and half the remaining measure of consumed oxygen represents the hydrogen; 5thly, the residuary gas after these processes is the nitrogen of the coal gas.

Structure of flame.—The quantity of light obtained from the combustion of coal gas depends entirely upon the manner in which it is burned, which will appear from the consideration of the structure of luminous flames. The flame of a spirit lamp, candle, or gas-jet is hollow, as may be observed by depressing a sheet of wire trellis upon it, which gives a section of the flame; the seat of the combustion being the margin of the flame, where alone the combustible vapour is in contact with the air. Of volatile carbonaceous combustibles, the flame consists of three parts, which are represented in section, (Fig. 44.):



A, cone of vaporized combustible.

B, sphere of partial combustion.

C, sphere of complete combustion.

In B, where the supply of air is insufficient for complete combustion, it is the hydrogen principally which burns, the carbon being liberated in solid particles, which are heated white-hot from the combustion of that gas. The sphere B, indeed, is the luminous portion of the flame, for the light depends entirely upon the deposition of carbon, arising from the consecutive combustion of the two elements of the vapour. Gaseous bodies, however strongly heated, emit no light, or at most, not more than a sensible glow, and luminous flame has justly been described by Davy as always containing *solid matter heated to whiteness*. The same sphere of the flame, possessing an excess of combustible matter at a high temperature, takes oxygen from metallic oxides, such as arsenious acid, placed in it, and develops their metals. It is, therefore, often referred to as the deoxidizing or reducing flame. In the external hollow cone, C, the deposited carbon meets with oxygen, and is entirely consumed. The hottest point in the whole flame is within this sphere, near the summit of B. This part of the flame, possessing an excess of oxygen, at a high temperature, is the proper place for kindling a combustible, and is called the oxidizing flame; its properties are the opposite of those of B.

When coal gas is mingled with an equal bulk of air before being burned, it is found to lose half its illuminating power. It may be conveniently mixed with a quantity of air sufficient for its complete combustion, by placing over an argand burner, a brass chimney of 5 inches in height, provided with a cap of wire gauze; when kindled above the wire-gauze, the gas burns with a blue flame, not more luminous than that of sulphur. The flame is so feebly luminous because no deposition of carbon occurs in it. The quantity of heat is the same, whether the gas is burned so as to produce much or little light; and where the gas is burned for heat, this mode of combustion has the advantage of giving a flame without smoke. The heat derived from coal gas burned in this manner is not, however, so intense as that of an argand spirit lamp. According to my own experience, the highest temperature is obtained from coal gas, when burned from that form of the argand recently introduced, in which the burner rises through a truncated brass cone. A tangential current of air is thus occasioned, which sweeps the outer surface of the flame, and produces a perfect combustion.

The burner should be provided besides with a metallic chimney of four inches in height, without the wire gauze.*

A result of the circumstances which determine the quantity of light from different flames is, that the larger the flame till it begins to be smoky, the greater the proportion of light obtained from the consumption of the same quantity of gas. It was observed that an argand burner, supplied with $1\frac{1}{2}$ cubic feet of gas per hour, gave as much light as a single candle; with 2 cubic feet per hour the light was equal to 4 candles, and with 3 cubic feet to 10 candles. Hence argands, bat-wings and other burners, in which a considerable quantity of gas is burned together, are more economical than plain jets. The brightness of ordinary flame, which depends essentially upon the consecutive combustion of hydrogen and carbon, is increased by everything which promotes the rapidity and intensity of the combustion, without deranging the order of oxidation, such as a rapid supply of air, and the substitution of pure oxygen for air, as in Mr. Gurney's Bude light. Not only is there then more light, because there is more combustion in the same time, but the temperature of the flame being greater, the luminous carbon is also heated to a higher degree of whiteness.

Olefiant gas, C_4H_4 or C_4H_3 , H.—This gas was discovered in 1796, by certain associated Dutch chemists, who gave it the name of olefiant gas, because it forms with chlorine a compound, having the appearance of an oil, from which the chlorides of carbon were afterwards derived (page 375.) This gas is prepared by heating together 1 measure of strong alcohol with 3 measures of oil of vitriol, in a capacious retort, till the liquid becomes black and effervescence begins, and maintaining it at that particular temperature. It is collected over water, which deprives it of a portion of ether vapour and sulphurous acid, with which it is accompanied. Olefiant gas burns with a white flame, and contains a large quantity of combustible matter in a given volume. It consists of 8 volumes of carbon vapour and 8 of hydrogen, condensed into 4 volumes, which gives for its density 981. It is now viewed as a compound of the organic radical acetyl with hydrogen, which is expressed in the rational formula stated above. Several other compounds of carbon and

* The form of argand recommended is known as the patent double-cone gas burner.

hydrogen exist, but they will be studied with most advantage under organic chemistry, to which they properly belong.

SECTION II.

CARBON AND SULPHUR.

Bisulphuret of carbon, $C S_2$.—Charcoal ignited in an atmosphere of sulphur vapour, combines with that element, and forms a compound which holds the same place in the sulphur series that carbonic acid occupies in the oxygen series of compounds. The bisulphuret of carbon is a volatile liquid, and may be prepared by distilling, in a porcelain retort, yellow pyrites or bisulphuret of iron, with a fourth of its weight of well-dried charcoal, both in the state of fine powder and intimately mixed. The vapour from the retort is conducted to the bottom of a bottle filled with cold water, to condense it. Or sulphur vapour may be sent over fragments of well dried charcoal in a porcelain or cast iron (not malleable iron) tube, placed across a furnace. The product is generally of a yellow colour, and contains sulphur in solution, to free it from which it is redistilled in a glass retort, by a gentle heat.

The bisulphuret of carbon is a colourless liquid, of high refracting power, and sp. gr. 1.272. Its vapour has a tension of 7.38 Paris inches (Marx) at 50° , and the liquid boils at 110° ; a cold of -80° can be produced by its evaporation in vacuo. This compound is extremely combustible, taking fire at a temperature which scarcely exceeds the boiling point of mercury. When a few drops of the liquid are thrown into a bottle of oxygen gas, or nitric oxide, a combustible mixture is formed, which burns, when a light is applied to it, with a brilliant flash of flame, but without a violent explosion. The bisulphuret of carbon is insoluble in water, but it is soluble in alcohol. It dissolves sulphur, phosphorus and iodine.

The bisulphuret of carbon is a sulphur acid, and combines with sulphur bases, such as the sulphuret of potassium, forming a class of salts which are called sulphocarbonates. Oxygen bases dissolve it slowly, and are converted into a mixture of carbonate and sulphocarbonate; thus 2 equivalents of potash with 1 of bisulphuret of carbon yield 2 equivalents of sulphuret

of potassium and 1 of carbonic acid, which combine respectively with bisulphuret of carbon and potash.

Solid sulphuret of carbon.—The charcoal left in the tube, after the process for the former compound, is much corroded, and contains a portion of sulphur which cannot be expelled from it by heat. Berzelius is disposed to consider this sulphur as in chemical combination with the carbon.

SECTION III.

CARBON AND NITROGEN.

Bicarburet of nitrogen, or cyanogen, N C_2 .—This compound is a gas, which was first obtained by Gay-Lussac in 1815. It is prepared by heating the cyanide of mercury in a small glass retort, and is collected at the mercurial trough. The cyanide is resolved into running mercury and cyanogen gas, and frequently leaves a black coaly mass in the retort, which Professor Johnston has shown to consist of carbon and nitrogen, in the same proportions as the gas itself.

Cyanogen gas contains 4 volumes of carbon vapour and 2 volumes of nitrogen, condensed into 2 volumes; its density is 1819. When this gas is exploded with twice its volume of oxygen, it affords 2 volumes of carbonic acid gas, and 1 volume of nitrogen, an experiment from which its composition may be deduced. Water at 60° absorbs 4.5 times its volume of this gas, and alcohol 23 volumes. By a pressure of 3.6 atmospheres at 45° , cyanogen is condensed into a limpid liquid, which evaporates again on removal of the pressure. Cyanogen burns with a beautiful purple flame in air or oxygen. The solution of cyanogen in water undergoes spontaneous decomposition. By alkalies the gas is absorbed, and a cyanide and cyanate formed.

Cyanogen is a salt-radical, and unites with all the metals, as chlorine and iodine do, forming a class of cyanides. It also forms a hydrogen acid, namely, prussic or hydrocyanic acid. Cyanogen properly belongs to organic chemistry, in which department its numerous combinations will be considered.

Mellon, $\text{N}_4 \text{C}_6$.—This is another salt-radical, and was formed by Liebig by heating the bisulphuret of cyanogen to redness, when it is resolved into sulphur, bisulphuret of carbon, and mellon. It is a lemon yellow powder, insoluble in water and alcohol. It unites directly with hydrogen and with potassium, forming hydromellonic acid and mellonide of potassium.

CHAPTER IV.

COMPOUNDS OF PHOSPHORUS.

Sulphuret of phosphorus.—Phosphorus and sulphur unite in all proportions, with the evolution of much heat, and sometimes with explosion. These elements are most safely united under hot water, of which the temperature, however, must not exceed 160° , for otherwise sulphuretted hydrogen and phosphoric acid may be produced with such rapidity as to occasion an explosion. The compounds of phosphorus and sulphur obtained in this manner appear not to be definite. They are more fusible and more inflammable than phosphorus itself. Levol has shown that they often contain a little of the persulphuret of hydrogen.* Serullas appears to have formed a definite sulphuret of phosphorus, by acting upon the liquid terchloride of phosphorus by sulphuretted hydrogen. Hydrochloric acid was evolved, and a solid amorphous body, of a lemon-yellow colour remained, which was a tersulphuret of phosphorus, corresponding with phosphorous acid. Berzelius ascertained that the sulphurets of phosphorus combine with sulphur bases, and produce colourless salts; but he did not carry the investigation beyond that point.

Phosphuret of nitrogen, N_2P .—Both the chlorides of phosphorus absorb ammoniacal gas, and form solid white compounds. The combination of the terchloride contains $2\frac{1}{2}$ equivalents of ammonia, but that of the perchloride, Rose did not find equally definite. When exposed to a strong red heat, without access of oxygen, these compounds leave a white amorphous body, which is the phosphuret of nitrogen.† It is most easily prepared by transmitting a stream of dry carbonic acid gas over the ammoniacal compound, in a tube of hard glass, heated by a charcoal fire, so long as vapours of sal ammoniac sublime.

The phosphuret of nitrogen is not soluble in any menstruum, nor acted upon by dilute acid or alkaline solutions. It is not

* An. de Ch. et de Ph. t. 67, p. 332.

† Rose, *Ib.* t. 54, p. 275.

affected when heated in an atmosphere of chlorine or sulphur, but is decomposed when heated in hydrogen, with the formation of ammoniacal gas. The want of volatility and indifference to most chemical reagents, which characterize this compound, are properties that could not have been anticipated in a compound of phosphorus and nitrogen.

CHAPTER V.

METALLIC ELEMENTS.

GENERAL OBSERVATIONS.

The metallic class of elements is considerably more numerous than the non-metallic class, embracing forty-two elementary bodies. Of these, seven only were known to the ancients, and of the remainder, a large proportion are of recent discovery. Their names and their densities, when accurately determined, with the dates and authors of their discovery, are contained in the following table, compiled from the work of Dr. Turner:—

TABLE OF METALS.

Name.	Density.	Dates and Authors of the Discovery.
Gold . . .	19.257, Brisson .	Known to the Ancients.
Silver . . .	10.474, ditto .	
Iron . . .	7.788, ditto .	
Copper . . .	8.895, Hatchett .	
Mercury . .	13.568, Brisson .	
Lead . . .	11.352, ditto .	
Tin . . .	7.291, ditto .	
Antimony . .	6.702, ditto .	1490, Described by Basil Valentine.
Bismuth . . .	9.822, ditto .	1530, Described by Agricola.
Zinc . . .	6.861 to 7.1, ditto	16th century, first mentioned by Paracelsus.
Arsenic . . .	5.884, Turner .	1733, Brandt.
Cobalt . . .	8.538, Haüy .	
Platinum . .	20.98, Brisson .	1741, Wood, assay-master, Jamaica.
Nickel . . .	8.279, Richter .	1751, Cronstedt.
Manganese . .	6.850, Bergman .	1774, Gahn and Scheele.
Tungsten . .	17.6, D'Elhuyart .	1781, D'Elhuyart.
Tellurium . .	6.115, Klaproth .	1782, Müller.
Molybdenum .	7.400, Hielm .	1782, Hielm.
Uranium . . .	9.000, Bucholz .	1789, Klaproth.
Titanium . .	5.3, Wollaston .	1791, Gregor.
Chromium	1797, Vauquelin.
Columbium	1802, Hatchett.
Palladium . .	11.3 to 11.8, Wollaston	1803, Wollaston.
Rhodium	1803, Descotils and Smithson Tennant.
Iridium	
Osmium	
Cerium	
Potassium . .	0.865 { Gay-Lussac	1807, Davy.
Sodium . . .	0.972 { and Thenard	
Barium	
Strontium	
Calcium	
Cadmium . . .	8.604 Stromeyer .	
Lithium	
Zirconium	1818, Stromeyer.
Aluminum	1818, Arfwedson.
Glucinum	1824, Berzelius.
Yttrium	1828, Wöhler.
Thorium	
Magnesium	1829, Berzelius.
Vanadium	1829, Bussy.
Lanthanum	1830, Sefström.
		1839, Mosander.

Of the physical properties of metals and their combinations with each other, the most characteristic is their lustre and power to reflect much of the light which falls upon them, a property exhibited in a high degree by burnished steel, speculum metal, and the reflecting surface of mercury in glass mirrors. Metals are also remarkable for their opacity, although they have a certain degree of transparency in a highly attenuated state, as fine gold-leaf allows light of a green colour to pass through it. They are peculiarly the conductors of electricity, and also the best conductors of heat. The most dense substances in nature are found among the metals, gold, for instance, being upwards of nineteen, and platinum nearly twenty-one times heavier than an equal bulk of water. But some of the metals, notwithstanding, are very light, potassium and sodium floating upon the surface of water.

Certain metals possess a valuable property, *malleability*, depending upon a high tenacity with a certain degree of softness; particularly gold, silver, copper, tin, platinum, palladium, cadmium, lead, zinc, iron, nickel, potassium, sodium, and solid mercury. These metals may all be hammered out into plates, or even into thin leaves. In zinc this property is found in the highest degree between 300° and 400° , and in iron at a degree of temperature exceeding a red heat. The same metals are likewise *ductile*, or may be drawn into wires, although the ductility of different metals is not always proportional to their malleability, iron being highly ductile, although it cannot be beaten into very thin leaves. By a peculiar method, Dr. Wollaston formed gold wire so small that it was only 1-5000th of an inch in diameter, and 550 feet of it were required to weigh one grain. He also obtained a wire of platinum not more than 1-30,000th of an inch in diameter*. The tenacity of different metals is determined by ascertaining the weight required to break wires of them having the same diameter. Iron appears to possess that property in the greatest, and lead in the least degree. It has been observed by M. Baudrimont that the tenacity of wires of iron, copper, and brass is much injured by annealing them†. A few of the malleable metals can be *welded*, or portions of them joined into one by hammering them together. Pieces of iron or platinum may be united in this

* Phil. Trans. 1813.

† An. de Ch. et de Ph. t. 60, p. 78.

manner at a bright red heat, and fragments of potassium may be made to adhere by pressing them together with the hand at the temperature of the air. Many metals are only malleable in a low degree, and some are actually brittle, such as bismuth, antimony, and arsenic.

The metals, with the exception of mercury, are all solid at the temperature of the air, but they may be liquefied by heat. Their points of fusion are very different, as will appear from the following table* :

TABLE OF THE FUSIBILITY OF DIFFERENT METALS.

		Fahr.	
Fusible below a red heat.	Mercury . . .	-39°	Different chemists.
	Potassium . . .	136	Gay-Lussac and Thenard.
	Sodium . . .	190	
	Tin . . .	442	Crichton.
	Bismuth . . .	497	
	Lead . . .	612	
	Tellurium—rather less fusible than lead.	.	Klaproth.
	Arsenic—undetermined.	.	
	Zinc . . .	773	Daniell.
	Antimony—a little below a red heat.	.	
Infusible below a red heat.	Cadmium . . .	442	Stromeyer.
	Silver . . .	1873	Daniell.
	Copper . . .	1996	
	Gold . . .	2016	
	Cobalt—rather less fusible than iron.	.	
	Iron, cast . . .	2786	Daniell.
	Iron, malleable	} Requiring the highest heat of a smith's forge.
	Manganese	
	Nickel—nearly the same as cobalt.	.	
	Palladium.	.	
	Molybdenum	{ Almost infusible, and not to be procured in buttons by the heat of a smith's forge.	} Fusible before the oxi-hydrogen blow-pipe.
	Uranium		
	Tungsten		
	Chromium	} Infusible in the heat of a smith's forge, but fusible before the oxi-hydrogen blow-pipe.	
	Titanium		
	Cerium		
	Osmium		
	Iridium		
	Rhodium		
	Platinum		
	Columbium		

The metallic elements are, in general, highly fixed substances, although it is probable that all of them may be dissipated at the highest temperatures. The following metals are so volatile as to be occasionally distilled,—cadmium, mercury, arsenic, tellurium, sodium, potassium and zinc.

* Dr. Turner's Elements of Chemistry, p. 414.

All the metals are capable of uniting with oxygen, but they differ greatly from each other in their affinity for that element. The greater number of them absorb oxygen from dry air at the usual temperature, and undergo oxidation, which is only slight and superficial in many, when they are in mass, but may be complete and perfect in the same metals, when they are highly divided, and in a favourable state for combination, as in the lead and iron pyrophorus exposed to air. The same metals exhibit, at a high temperature, a more intense affinity for oxygen, and combine with combustion. The only metals which do not unite with oxygen directly in any circumstances are silver, palladium, platinum, gold, and probably rhodium and iridium.

The metals have been arranged in six groups or sections, differing in their degrees of oxidability. 1. Metals which decompose water even at 32° , with lively effervescence, namely, potassium, sodium, lithium, barium, strontium, calcium, and probably magnesium. 2. Metals which do not decompose water at 32° , like the metals of the preceding class; they do not decompose it with a lively effervescence, except at a temperature approaching 212° or even higher, but always much below a red heat. In this class are found glucinum, aluminum, zirconium, thorium, yttrium, cerium, and manganese. 3. Metals which do not decompose water except at a red heat, or at the ordinary temperature with the presence of strong acids. This section comprehends iron, nickel, cobalt, zinc, cadmium, tin, chromium, and probably vanadium. Iron is rapidly corroded in water containing carbonic acid, with the evolution of hydrogen. 4. Metals which decompose the vapour of water at a red heat with considerable energy, but which do not decompose water in presence of the strong acids. They are tungsten, molybdenum, osmium, columbium, titanium, antimony, and uranium. These metals appear to be incapable of decomposing water in contact with acids, because their oxides have but a small basic power, being indeed bodies which are ranked among the acids. 5. Metals of which the oxides are not decomposed by heat alone, and which decompose water only in a feeble manner, and at a very high temperature. They are also distinguished from the preceding class by their tendency to form basic and not acid oxides. These metals are copper, lead, and bismuth. 6. Metals of which the oxides are reducible by

heat alone at a temperature more or less elevated; these metals do not decompose water in any circumstances. They are mercury, silver, palladium, platinum, gold, and probably rhodium and iridium*. It is to be remarked of nearly all the metals which decompose the vapour of water, and consequently separate hydrogen from oxygen at a certain temperature, that their oxides are reduced, notwithstanding, with great facility by hydrogen gas, and within the same limits of temperature. This anomalous result has already been adverted to in regard to iron (p. 188).

Of the thirteen non-metallic elements, hydrogen only forms a basic oxide capable of uniting with acids. It is a general character of the metals, on the contrary, to form such oxides, if tellurium be excepted, which is more analogous in its chemical properties to sulphur than to the metals. Hence, as the former class are principally salt-radicals, the latter are principally basyles.

The protoxides of metals are uniformly and strongly basic, but this feature becomes less distinct in their superior oxides, and passes into the acid character in the high degrees of oxidation of which some metals are susceptible. Thus, of manganese, the protoxide is a strong base, the deutoxide basic but in a less degree than the protoxide; the peroxide indifferent, and the still higher oxides are the manganic and hypermanganic acids, which are respectively isomorphous with sulphuric and hyperchloric acids. A few metals which have no protoxides, such as arsenic and antimony, are most remarkable for the acids they form with oxygen, and thus more resemble in their chemical history the elements of the non-metallic class. It is indeed impossible to draw an exact line of demarcation between the two classes of elements, either with reference to their physical or chemical properties.

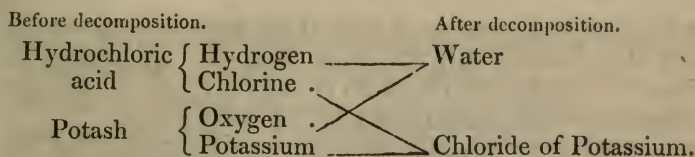
Besides combining with oxygen, metals combine with sulphur, chlorine, and with other salt-radicals, whether simple or compound, and hence sulphurets, chlorides, and numerous other series of metallic compounds. Of these series the sulphurets most resemble the oxides of the same metals; the chlorides and other series partake more strongly of the saline character. Each metal, or class of metals affects combination

* Régnault, *Ann. de Ch. et de Ph.* t. 62, p. 368.

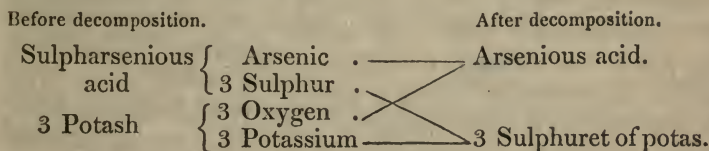
with oxygen in certain proportions, and combines also with sulphur, chlorine, &c., in the same proportions. Hence, given the formulæ of the oxides of a metal, the formulæ of its sulphurets, chlorides, &c., may generally be predicated, as they correspond with the former. Thus the oxides of iron being Fe O and $\text{Fe}_2 \text{O}_3$, the sulphurets are Fe S and $\text{Fe}_2 \text{S}_3$, and the chlorides Fe Cl and $\text{Fe}_2 \text{Cl}_3$; the oxides of arsenic, or arsenious and arsenic acids, being As O_3 and As O_5 , the sulphurets of that metal are As S_3 and As S_5 , and the chlorides As Cl_3 and As Cl_5 . But sometimes a metal unites with sulphur in more ratios than with oxygen, both iron and arsenic, for example, possessing each a sulphuret to which they have no corresponding oxide, namely martial pyrites and realgar, of which the formulæ are Fe S_2 and As S_2 . The potassium family of metals combine also with three and five equivalents of sulphur, without all uniting with oxygen in such high proportions. Again, certain metals of the magnesian and its allied families, such as manganese and chromium, form acid compounds with oxygen, to which no corresponding sulphurets exist, such as manganic and chromic acids, Mn O_3 and Cr O_3 . But the circumstance that these acids are isomorphous with sulphuric acid, and the metals they contain isomorphous with sulphur, appears to be a sufficient reason why there should not be similar sulphur acids. The chlorides of a metal generally correspond in number, as they always do in composition, with the oxides; in some cases they are less numerous, but never, I believe, more numerous than the oxides of the same metal.

Combination takes place within a series, that is, oxides combine with oxides, sulphurets with sulphurets. Those members of the same series which differ greatly in chemical characters being most disposed to combine together, as oxygen acids with oxygen bases, sulphur acids with sulphur bases. Chlorides also combine with chlorides, to form double chlorides, and iodides with iodides.

Compounds belonging to different series, on the contrary, do not combine together, but often mutually decompose each other, when brought into contact. Thus hydrochloric acid and potash do not unite, but form water and chloride of potassium, by mutual decomposition, as explained in the following diagram :—



In the same manner, peroxide of iron, dissolved in hydrochloric acid, produces water and a perchloride of iron corresponding with the peroxide: 3 H Cl and $\text{Fe}_2 \text{ O}_3 = 3 \text{ H O}$ and $\text{Fe}_2 \text{ Cl}_3$. And in all cases when a metallic oxide dissolves in hydrochloric acid, without evolution of chlorine, the chloride produced necessarily corresponds with the oxide dissolved. Again, orpiment, or sulpharsenious acid does not combine with potash, when dissolved in that alkaline oxide, but gives rise to the formation of certain proportions of arsenious acid, and sulphuret of potassium:—



Two pairs of compounds of different series then coexist in the liquid, an oxygen acid, arsenious acid, which unites with the oxygen base, potash, and a sulphur base, sulphuret of potassium, which unites with undecomposed sulpharsenious acid. Hence the result of dissolving orpiment in potash is the decomposition of both compounds and formation of two salts of different series, arsenite of potash and sulpharsenite of sulphuret of potassium.

The union of metallic compounds of the oxygen and sulphur series is a rare occurrence. But the red ore of antimony is such a combination, and oxisulphurets of mercury also exist. Compounds of metallic oxides with metallic chlorides, and with other highly saline binary compounds, are more frequent; but they are not to be placed in the same category with the compounds of individuals both belonging to the same series, which last are neutral salts. For a metallic oxichloride may generally, if not always, be viewed as a chloride to which a certain proportion of metallic oxide is attached, like constitutional water in a hydrated salt. That metallic oxide is likewise always of the magnesian class, or of a class allied to it. Oxichlo-

rides are then to be associated with those salts of oxygen-acids usually denominated subsalts (page 169); the oxichlorides of lead and of copper, $\text{Pb Cl} + 3 \text{ Pb O}$ and $\text{Cu Cl} + 3 \text{ Cu O}$, with the subacetates and subsulphates of the same metals.

Arrangement of metallic elements.—A distribution of the metals into three classes is generally made, composed respectively of the metals of the alkalis and alkaline earths, the metals of the earths, and the metals proper. The latter class again is subdivided, according to the affinity of the metals contained in it for oxygen, into the two groups, the noble and common metals, the oxides of the former, such as gold, silver, &c., abandoning their oxygen at a high temperature, while the oxides of the latter, lead, copper, &c., are undecomposable by heat alone. In treating of the metals, I shall introduce them in the order which appears to facilitate most the study of their combinations, with a general reference to that old classification. For subdivisions, I shall avail myself of the natural families into which the elements have been arranged (page 142), which have the advantage of bringing together those metals of which the compounds are most frequently isomorphous. The different metals will therefore be grouped under the following heads:—

I. Metallic bases of the alkalis—three metals:

	Oxides.
Potassium . . .	Potash.
Sodium . . .	Soda.
Lithium . . .	Lithia.

II. Metallic bases of the alkaline earths—four metals:

	Oxides.
Barium . . .	Barytes.
Strontium . . .	Strontian.
Calcium . . .	Lime.
Magnesium . . .	Magnesia.

III. Metallic bases of the earths proper—five metals:

	Oxides.
Aluminum . . .	Alumina.
Glucinum . . .	Glucina.
Zirconium . . .	Zirconia.
Yttrium . . .	Yttria.
Thorium . . .	Thorina.

IV. Metals proper, of which the protoxides are isomorphous with magnesia, with bismuth—nine metals :

Manganese.	Cadmium.
Iron.	Copper.
Cobalt.	Lead.
Nickel.	Bismuth.
Zinc.	

V. Other metals proper having isomorphous relations with the magnesian family—seven metals :

Tin.	Tungsten.
Titanium.	Molybdenum.
Chromium.	Tellurium.
Vanadium.	

VI. Metals isomorphous with phosphorus—two metals :

Arsenic.	Antimony.
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VII. Metals proper, not included in the foregoing classes, of which the oxides are not reduced by heat alone—four metals :

Uranium.	Lanthanum.
Cerium.	Columbium or Tantalum.

VIII. Metals proper, of which the oxides are reduced to the metallic state by heat, (noble metals)—three metals :

Mercury.	Gold.
Silver.	

IX. Metals peculiar to native platinum (noble metals)—five metals :

Platinum.	Osmium.
Palladium.	Rhodium.
Iridium.	

ORDER I.

METALLIC BASES OF THE ALKALIES.

SECTION I.

POTASSIUM.

Syn. KALIUM. *Eq.* 490 or 39.3; K.

The alkalies and earths have long been named and distinguished from each other, but they were not known to be the oxides of peculiar metals till a recent period. The terms ap-

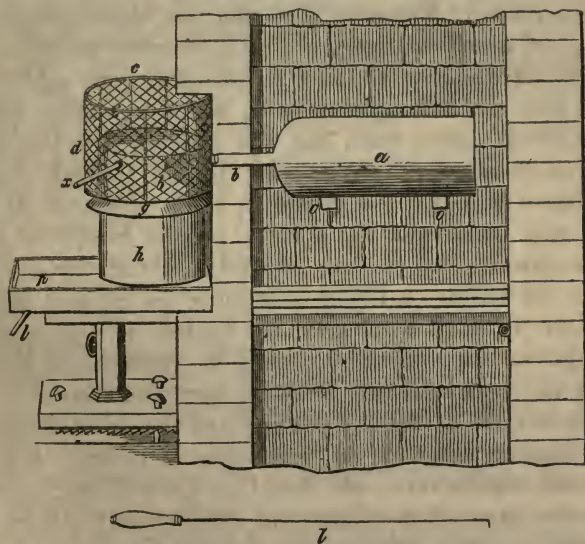
plied to the new metallic bases are formed from the names of their oxides, as potassium from potash, and calcium from calx, a name sometimes given to lime; while the original names of the oxides are still retained, as those of ordinary objects, and not superseded by appellations indicating their relation to the metals, such as oxide of potassium for potash, or oxide of calcium for lime.

Preparation.—In 1807, Sir H. Davy made the memorable discovery that potash is resolved by a powerful voltaic battery into potassium and oxygen. He placed a moistened fragment of hydrate of potash upon mercury, introducing the terminal wire from the zinc extremity of an active battery (the chloroid) into the fluid metal, and touching the potash with the other terminal wire (the zincoïd); bubbles of oxygen gas appeared at the latter wire, and potassium was liberated at the former, and dissolving in the mercury, was protected from oxidation by the air. To effect this decomposition, Davy employed a battery of 200 pairs of four-inch plates; but an amalgam of potassium may be as readily obtained by a more simple voltaic apparatus, in the manner described at page 239. These processes, however, afford potassium only in minute quantity. Soon after the existence of this metal was known, Gay-Lussac and Thenard discovered that potash is decomposed by iron at a white heat, and they contrived a process by which a more abundant supply of the metal was obtained. It was afterwards noticed by Curaudau that potash, like the oxides of common metals, is decomposed by charcoal as well as by iron, which is the basis of the process for potassium now always followed.

This interesting and useful process is described by Mitscherlich, as it is successfully pursued in Germany. Whenever charcoal is used to deprive a metallic oxide of its oxygen, the former must be in a state of minute division, and be intimately mixed with the latter. Carbonate of potash requires this precaution the more, that it fuses at a red heat, and is thus apt to separate from the charcoal, and sink below it. It is found that the best means to obtain a proper mixture of these substances is to calcine a salt of potash containing a vegetable acid, which leaves a large quantity of charcoal, when decomposed. Crude tartar (bitartrate of potash) is preferred, and for one operation six pounds of that salt are ignited in a large crucible or melting-pot provided with a lid, so long as combustible gases are dis-

engaged. The crucible is then withdrawn from the fire, and is found to contain a black mass, which is the mixture of charcoal and carbonate of potash, known as black flux. It is reduced to powder, while still warm, and immediately mixed with about ten ounces of wood-charcoal in small pieces, or in a coarse powder, from which the dust has been separated by a sieve. The use of this additional charcoal is to act as a sponge, and absorb the potash when liquefied by heat. The mixture is introduced into a bottle of wrought iron, and a mercury bottle (page 244) answers well for the purpose, but must be heated to redness before hand, to expel a little mercury that remains in it. The mouth of the bottle is enlarged a little by means of a round file, and a straight iron tube of 4 or 5 inches in length fitted into the opening, by grinding. The bottle and tube thus form a retort, which is supported horizon-

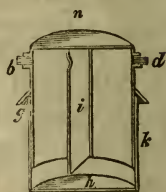
FIG. 45.



tally in a brick furnace, as represented (Fig. 45) in which *a* is the iron bottle resting upon two bars of iron *o o*, to which it may also be firmly bound by iron wire. These bars cross the furnace at a height of 5 or 6 inches above the grate-bars. A mixture of equal parts of coal and coke makes an excellent fuel for this furnace. The tube *b* of the bottle projects through

an aperture in the side-wall of the furnace, and enters a receiver of a peculiar construction required to condense the potassium, which distils over. This receiver is composed of two separate copper cylinders or oval boxes, hard soldered, similar in form and size, which are represented in section in figure 46, the one *b n d* being introduced within the other *g h k*, and thus forming together a vessel of which *b n d* is the cover. It will also be observed that *b n d* is divided into two cells by a diaphragm *i*, of the same length as the cylinder, and descending with it to within two inches of the bottom *h* of *g h k*. A ribbon of copper *g* is soldered around *b n d*, so as to form a ledge, which is seen in both figures, and serves as a support for a cage of iron-wire *c d*, placed over the receiver during the distillation, to hold ice, and also to shed the water from the liquefaction of that ice, which falls into a tray *p* below, and flows off by the tube *l*. The cover has also two short copper tubes *d* and *b*, of which the copper of *b* is notched so as to clasp firmly by its elasticity the tube *b* from the iron bottle, which is fitted into it. The other tube *d*, which is exactly opposite to *b*, is fitted with a cork, and the diaphragm *i* has a small hole in it to allow of a rod being passed through *b* and *d*. In the same part of the apparatus is a third opening, to which a glass tube *x* is fitted by a cork, for the escape of uncondensable gases. The receiver is filled to about one-third with rectified petroleum, a liquid containing no oxygen, so as to come near to, but not to cover the bottom of the partition *i*. The length of the bottle is 11 inches, its width 4, and the other parts of the apparatus are designed upon the same scale.

FIG. 46.



Potassium and carbonic oxide gas are the principal products of the decomposition of the carbonate of potash, but other substances besides these are found in the receiver, namely, a black mass very rich in potassium, some oxalate and croconate of potash and free potash, with a portion of charcoal powder carried over mechanically. Part of these products appear to be formed, after the reduction of the potassium, by the mutual reaction of that metal, carbonic oxide and petroleum. The process is found to succeed best when the iron tube *b* is so short that it can be maintained at a red heat through its whole length during the operation, while the receiver is kept at a very low

temperature; the potassium then falls from the tube, drop by drop, into the receiver, and does not remain long in contact with carbonic oxide, which is known to combine readily with that metal. One or two other points should also be attended to. The connexion between the tube *b* and the receiver is not made till the iron bottle has been heated to redness, to allow of the escape of a little water, and of a trace of mercury, which had remained in the bottle in the state of vapour, and which come off first. The joining of the tube *b* is not air-tight at first, and allows a little potassium vapour to escape, but this burns and forms potash, which immediately closes the openings. This tube being always incandescent, and the refrigeration properly made, the reduction sometimes proceeds without interruption. But the tube is sometimes obstructed, as appears by the gases ceasing to escape by *x*. Haste must then be made to open the tube *b*, and to clear it by means of a flattened iron rod *l*, slightly hooked at its anterior extremity. Care has been taken to mark on this rod, with the scratch of a file, how far it has to penetrate into the apparatus to reach the mouth of the bottle, and it must not be introduced farther. The current of air through the furnace is regulated by a register valve in the chimney, and the fire stirred frequently so as to prevent the formation of cavities; the operator being guided in the management of the fire by the rapidity of the current of gas which escapes by the tube *x*. To terminate the operation, the grate bars may be thrown down, by which the fuel will fall into the ash-pit. The quantity of crude tartar mentioned yields about 4 ounces of potassium, which is about 4 per cent of its weight. The potassium thus obtained, containing a little carbon chemically combined with it, is submitted, together with the black mass found in the receiver, to a second distillation. For this purpose a smaller iron bottle with a bent tube may be employed, the end of which is covered by rectified petroleum in a capacious flask, used as a receiver.*

Properties.—Potassium is solid at the usual temperature, but so soft as to yield like wax to the pressure of the fingers. A fresh surface has a white colour, with a shade of blue, like steel, but is almost instantly covered by a dull film of oxide, when exposed to air. The metal is brittle at 32°, and has been observed crystallized in cubes: it is semi-fluid at 70°,

* Mitscherlich, *Elémens de Chimie*, t. 3, p. 8.

and becomes completely liquid at 150° . It may be distilled at a low red heat, and forms a vapour of a green colour. Potassium is considerably lighter than water, its density being 0.865 at 60° .

Potassium oxidates gradually without combustion when exposed to air, but heated till it begins to vaporise, it takes fire and burns with a violet flame. The avidity of this metal for oxygen is strikingly exhibited when a fragment of it is thrown upon water. It instantly decomposes the water, and so much heat is evolved as to kindle the potassium, which moves about upon the surface of the water, burning with a strong flame, of which the vivacity is increased by the combustion of the hydrogen gas disengaged at the same time. A globule of fused potash remains, which continues to swim about upon the surface of the water for a few seconds, but finally produces an explosive burst of steam, when its temperature falls to a certain point, illustrating the phenomenon of a drop of water on a hot metallic plate (page 47.)

Potassium appears to have the greatest affinity of all bodies for oxygen, at temperatures which are not exceedingly elevated. It decomposes nitrous and nitric oxides, and also carbonic oxide gas at a red heat, although potash is reduced to the metallic state by charcoal at a white heat. It has already been stated that the oxides and fluorides of boron and silicon are decomposed by potassium, and besides these elements, several of the metallic bases of the earths are obtained by means of this metal. It is indeed a reducing agent of the greatest value.

COMPOUNDS OF POTASSIUM.

Potash or potassa; KO ; 590 or 47.26.—Potassium exposed in thin slices to dry air becomes a white matter, which is the protoxide of potassium or potash. This compound is fusible at a red heat, and rises in vapour at a strong white heat. It unites with water, with ignition, and forms a fusible hydrate, which is the ordinary condition of caustic potash.

The hydrate of potash is obtained in quantity from the carbonate of potash. Equal weights of that salt and of quicklime are taken, the latter of which is slaked with water, and falls into a powder consisting of hydrate of lime; the former is dissolved in from 6 to 10 times its weight of water, and both

boiled together for half an hour in a clean iron pan. The lime abstracts carbonic acid from the potash, and becomes carbonate of lime; a reaction which may be illustrated by adding lime-water to a solution of carbonate of potash, when a precipitate of carbonate of lime falls. When the potash has been deprived entirely of carbonic acid, a little of the clear liquid taken from the pan will be found not to effervesce upon the addition of an acid to it. It is remarkable that the decomposition is never complete, if the carbonate of potash be dissolved in less than the prescribed quantity of water. Liebig has observed that a concentrated solution of potash decomposes carbonate of lime, and consequently hydrate of lime could not, in the same circumstances, decompose carbonate of potash. The pan being covered by a lid, may be allowed to cool; as the insoluble carbonate of lime and the excess of hydrate of lime subside, a considerable quantity of the clear solution of potash may be drawn off by a syphon, and the remainder may be obtained clear by filtration. In the latter operation a large glass funnel may be employed, to support a filter of washed cotton calico, into which what remains in the pan is transferred. A small portion of liquid, which passes through turbid at first, should be returned to the filter. As the solution of potash absorbs carbonic acid, it is proper to conduct its filtration with as little exposure to air as possible; on which account the mouth of the funnel should be covered by a plate, and the liquid which flows from it be immediately received in a bottle, in the mouth of which the funnel may be supported. The bottle in which potash is preserved should not be of crystal, or of a material containing lead, as the alkali corrodes such glass, particularly when its natural surface has been cut.

To obtain the solid hydrate of potash, the preceding solution is rapidly evaporated in a clean iron pan or silver bason, till an oily liquid remains at a high temperature, which contains no more than a single equivalent of water. This liquid is poured into cylindrical iron moulds, to obtain it in the form of sticks, which are used by surgeons as a cautery, and are the *potassa* or *potassa fusa* of the pharmacopeia; a form in which it is also convenient to have potash for some chemical purposes. The sticks generally contain a portion of carbonate of potash, besides a little oxide of iron and peroxide of potassium, the last of which gives occasion to the evolution of a little oxygen gas

when the sticks are dissolved in water. To obtain hydrate of potash free from carbonate, the sticks are dissolved in alcohol, in which the foreign impurities are insoluble, and the alcoholic solution is evaporated to dryness.

The pure and fused hydrate of potash is a solid white mass of a structure somewhat crystalline, of sp. gr. 1.706, fusible at a heat under redness. It is a protohydrate, and cannot be deprived of its combined water by the most intense heat. It destroys animal textures. It rapidly deliquesces in damp air, from the absorption of moisture, is soluble in half its weight of water, and also in alcohol. Mixed in powder with a small quantity of water, it forms a second crystalline combination, which is a terhydrate; and its solution in water affords, at a very low temperature, crystals in the forms of four-sided tables and octohedrons, which are a pentahydrate, $\text{KO}, \text{HO} + 4 \text{HO}$.

The solution of potash, or potash ley, has a slight but peculiar odour, characteristic of caustic alkalies, which they acquire from their action upon organic matter, derived from the atmosphere or other sources. The skin and other animal substances are dissolved by this liquid. It is highly caustic, and its taste intensely acrid. It has those properties which are termed alkaline in an eminent degree. It neutralises the most powerful acids, restores the blue colour of reddened litmus, changes the blue infusion of cabbage into green, but in a short time altogether destroys these vegetable colours. It acts upon fixed oils, and converts them into soaps, which are soluble in water. It absorbs carbonic acid with great avidity from the air, on which account it should be preserved in well stoppered bottles.

The presence of free potash or soda, in solutions of their carbonates, may be discovered by nitrate of silver, the oxide of which is precipitated of a brown colour by the caustic alkali, while the white carbonate of silver only is precipitated by the pure carbonated alkali. Potash, whether free, or in combination with an acid as a soluble salt, may be detected and distinguished from soda and all other substances, by means of certain acids, &c., which form sparingly soluble compounds with that alkali. A strong solution of tartaric acid produces a precipitate of bitartrate of potash, in a liquid containing 1 per cent of any potash salt. The precipitate is crystalline, and does not appear immediately, but is thrown down on stirring the liquid

strongly, and soonest upon the lines, which have been described on the glass by the stirrer. A similar precipitation is occasioned in salts of potash by hyperchloric acid. Also by chloride of platinum, which forms the double chloride of platinum and potassium, in granular octohedrons of a pale yellow colour. In the separation of potash, for its quantitative estimation, the last reagent is preferred, and is added in excess to the potash solution, together with a few drops of hydrochloric acid, which is then evaporated by a steam heat to dryness. Water with an admixture of alcohol is digested upon the dry residue, which dissolves up every thing except the double chloride of platinum and potassium. Ammonia is also thrown down by chloride of platinum; but when the chloride of platinum and ammonium is heated to redness, nothing is left except spongy platinum, while the chloride of platinum and potassium leaves all its potassium in the state of chloride mixed with the platinum. Potash is likewise separated from acids, by means of fluosilicic acid, which throws down a light gelatinous precipitate, the double fluoride of silicon and potassium.

Potash is the base which in general exhibits the highest affinity for acids; it precipitates lime and the insoluble metallic oxides from their solutions in acids. This alkali is employed indifferently with soda for a variety of useful purposes. The principal combinations of potash with acids will be described after the binary compounds of potassium.

Peroxide of potassium, KO_3 .—Heated strongly in air or oxygen, potassium combines with three equivalents of oxygen. The ultimate residue on calcining nitrate of potash at a red heat has been said to be the same compound, but Mitscherlich finds that residue to be potash. The peroxide of potassium is decomposed by water, being converted into hydrate of potash, with evolution of oxygen gas.

When potassium is burned with an imperfect supply of air, a grey matter is formed, which Berzelius believes to be a suboxide of potassium. It is not more stable than the peroxide.

Sulphurets of potassium.—Sulphur and potassium, when heated together, unite with incandescence, and in several proportions, two of which correspond respectively with the protoxide and peroxide of potassium. The *protosulphuret* may be obtained by transmitting hydrogen gas over sulphate of potash, heated in a bulb of hard glass to full redness, when the whole

oxygen of the salt is carried off as water, and the sulphur remains in combination with potassium, forming a fusible compound of a light brown colour. Sulphate of potash calcined with one-fourth of its weight of pounded charcoal or pit-coal, in a covered cornish crucible, at a bright red heat, is converted into a black crystalline mass, which is also proto-sulphuret of potassium, with generally a small quantity of a higher sulphuret, arising from the combination of the silica of the crucible with potash of the sulphate. If lamp-black be used instead of charcoal, the sulphuret of potassium formed having a great affinity for oxygen, and being in a highly divided state, takes fire, when exposed to the air, and forms a pyrophorus. The solution of the protosulphuret in water is highly caustic; it is decomposed by acids with effervescence, from the escape of sulphuretted hydrogen gas, but without any deposit of sulphur. Being a sulphur base, it combines without decomposition with sulphur acids.

This sulphuret unites directly with sulphuretted hydrogen; and the same compound may be otherwise formed, namely, by transmitting a stream of sulphuretted hydrogen through caustic potash, so long as the gas is absorbed. It is often named the *bihydrosulphuret of potash*. It is analogous in composition to hydrate of potash in the oxygen series.

The *Tritosulphuret* is formed when anhydrous carbonate of potash, mixed with half its weight of sulphur, is maintained at a low red heat so long as carbonic acid gas comes off. Of four proportions of potash, three become sulphuret of potassium, while sulphuric acid is formed which neutralises the fourth proportion of potash: 4KO and $10\text{S} = 3\text{KS}_3$ and KO, SO_3 . With carbonate of potash and sulphur, in equal weights, a similar action occurs, at a temperature above the fusing point of sulphur, but five, instead of three, proportions of sulphur then unite with one of potassium, and a *Pentasulphuret* is formed. With a larger proportion of carbonate of potash the same sulphuret is also produced, provided the temperature does not much exceed the boiling point of sulphur, and the excess of carbonate fuses along with it, without undergoing decomposition. A sulphuret obtained by fusing sulphur and carbonate of potash together has a liver-brown colour, and hence its old pharmaceutical name *Hepar sulphuris*. The three sulphurets described are deliquescent, and are all soluble in water, the higher sul-

phurets giving red solutions. They may indeed be prepared by boiling sulphur, in proper proportions, with caustic potash. A simultaneous formation of hyposulphurous acid then occurs, as already explained (page 331.) The preparation, *Precipitated sulphur*, is obtained by adding an excess of hydrochloric acid to these solutions, when much sulphur is thrown down, although the potassium be only in the state of protosulphuret, for the sulphuretted hydrogen arising from the action of the acid on that sulphuret, meets sulphurous evolved at the same time from the decomposition of hyposulphurous acid, and these gases mutually decompose each other, with the formation of water and sulphur. The excess of sulphur in the alkaline sulphuret also precipitates at the same time. The peculiar whiteness of precipitated sulphur is owing, according to Rose, to its containing a little persulphuret of hydrogen.

Chloride of potassium; K Cl ; 932.6 or 74.7.—Formed by the combustion of potassium in chlorine, or by neutralising hydrochloric acid by potash or its carbonate. It is also derived in considerable quantity from kelp (page 384.) It crystallizes in cubes and rectangular prisms, resembles common salt in taste, is soluble in 3 times its weight of water at 60° , and in less at 212° . When pulverised and dissolved in 4 times its weight of cold water, it produces a depression of temperature of $20\frac{1}{2}$ degrees; while chloride of sodium, dissolved in the same manner, lowers the temperature only 3.4 degrees. Upon the difference between the two salts in this property is founded a rude mode of estimating their proportions in a mixture. Chloride of potassium is principally consumed in the manufacture of alum.

Iodide of potassium; IK ; 2069.4 or 165.82.—This salt is obtained by dissolving iodine in solution of potash till neutral, evaporating to dryness, and heating to redness, to decompose the portion of iodate of potash formed. It is more soluble than the chloride, and may be obtained in cubes or rectangular prisms, which are generally white and opaque, and have an alkaline reaction from the presence of a trace of carbonate of potash. The dry salt does not combine with more iodine, but in conjunction with a small quantity of water, (I believe 4 equivalents) it absorbs the vapour of iodine with great avidity, and runs into a liquid of a deep red, almost black, colour. According to Baup, a saturated solution of iodide of potassium may dissolve

so much as two equivalents of iodine, but allows one equivalent to precipitate when diluted. Iodide of potassium is much used in medicine; it is not poisonous in doses of one or two drachms. Its solution is also employed as a vehicle for iodine itself, 20 grains of iodine, and 30 grains of iodide of potassium being usually dissolved in 1 ounce of water. The bromide of potassium is capable of dissolving bromine, but the solution of chloride of potassium has no affinity for chlorine.

Ferrocyanide of potassium, Yellow prussiate of potash; $K_2, Fe Cy_3 + 3HO$; 2308.7 + 337.5 or 185 + 27.—This important salt is formed when carbonate of potash is fused in an iron pot with animal matter, such as dried blood, hoofs, clippings of hides, &c., and is the product of a reaction to be hereafter described. This salt occurs in a state of great purity in commerce. It is of a lemon yellow colour, and crystallized in large quadrangular tables, with truncated angles and edges, belonging to the square prismatic system. The crystals contain 3 equivalents of water, which they lose at 212° , are soluble in 4 parts of cold and 2 parts of boiling water, and are insoluble in alcohol. The taste of this salt is saline, and it is not poisonous. By a red heat it is converted, with escape of nitrogen gas, into carburet of iron and cyanide of potassium; but with exposure to air the latter salt absorbs oxygen, and becomes cyanate of potash. This salt is represented by Liebig as containing a salt-radical, *Ferrocyanogen*, composed of 1 eq. of iron and 3 eq. of cyanogen, or $Fe Cy_3$. This imaginary radical is bibasic, and is in combination with 2 eq. potassium in the salt, as will be seen by reference to its formula. The same salt has been represented by myself as a compound of a tribasic salt-radical prussine ($3 Cy$) with $Fe + 2 K$. But its reactions with other salts are most easily stated on the former view of its constitution. The iron in this salt is not precipitated by alkalis. When ferrocyanide of potassium is added to salts of lead and various other metallic solutions, it produces precipitates, in which two atoms of the lead or other metal are substituted, in combination with ferrocyanogen, for the two atoms of potassium. In salts of peroxide of iron, ferrocyanide of potassium produces the well known precipitate prussian blue.

Ferricyanide of potassium, Red prussiate of potash; $3K, Fe_2 Cy_6$; 4127.6 or 331.74.—This salt, which like the last, is a valuable reagent, is formed by transmitting chlorine gas

through a solution of the ferrocyanide of potassium, till it no longer gives a precipitate of prussian blue with a persalt of iron. One fourth of the potassium of the ferrocyanide is converted into chloride, from which the resulting ferricyanide may be separated by crystallization. It forms right rhombic prisms, which are transparent and of a fine red colour. The crystals are anhydrous, soluble in 3.8 parts of cold, and in less hot water. They burn with brilliant scintillations when held in the flame of a candle. The solution of this salt is a delicate test of iron in the state of protoxide, throwing down from its salts a variety of prussian blue, in which the 3K of the formula are replaced by 3 Fe. Liebig views this salt as containing a salt-radical, *Ferricyanogen* or *ferridecyanogen*, $\text{Fe}_2 \text{Cy}_6$, differing from ferrocyanogen in having twice its atomic weight and being tribasic.

Cyanide of potassium; KCy, 819.8 or 65.69.—The preparation of this salt is attended with difficulty, owing to the action of the carbonic acid of the air upon its solution, which evolves hydrocyanic acid, and the tendency of the solution itself to undergo spontaneous decomposition, even in close vessels. It may be formed by adding absolute hydrocyanic acid, or a strong solution of that acid, to a solution of potash in alcohol; a portion of the cyanide falls down as a white crystalline precipitate, which should be washed with alcohol and dried, and an additional quantity is obtained by evaporating the liquid in a retort. But it is prepared with more advantage from the ferrocyanide of potassium already described. That salt is carefully dried and reduced to a fine powder, which is exposed to a strong red heat in a well closed iron crucible, or other convenient vessel, and then allowed to cool completely without exposure to air. The porous, semifused mass, which is a mixture of cyanide of potassium and carburet of iron, is reduced to a fine powder, placed in a funnel, moistened with a little alcohol, and then washed with cold water. The first strong solution of cyanide of potassium which comes through is colourless, and must be rapidly evaporated to dryness in a porcelain bason, and fused at a red heat. Or, alcohol of sp. gr. 0.896 (60 per cent) may be boiled upon the black mass, and dissolves a large quantity of cyanide, the greater proportion of which it deposits again on cooling, a property peculiar to alcohol of the strength prescribed. The application of hot water to the black mass is to be avoided, as with access of air, it causes the reproduction of

the ferrocyanide, which immediately colours the solution yellow (Liebig.)

The cyanide of potassium crystallizes in colourless cubes, which become opaque and deliquesce in damp air, and are very soluble in water. It bears a red heat without decomposition in close vessels, but with exposure to oxygen becomes cyanate of potash (KO , Cy O). Its solution smells of hydrocyanic acid, being decomposed by carbonic acid. The action of cyanide of potassium upon the animal economy is equally powerful with that of hydrocyanic acid, and as the dry salt may be preserved in a well stopt bottle without change, it is preferable to the acid, which is far from stable. Red oxide of mercury dissolves freely in the solution of cyanide of potassium, cyanide of mercury being formed and potash set free. The purity of the alkaline cyanide may be ascertained from this property; 12 grains of the pure cyanide dissolving 20 grains of finely pulverised oxide of mercury.

Hydrocyanic acid for medical purposes is conveniently prepared from this cyanide. 24 grains of cyanide of potassium, 56 grains of tartaric acid in crystals, and 1 ounce of water are agitated together in a stout phial closed by a cork. The liquid is afterwards separated by filtration from the precipitate of bitartrate of potash; it contains 10 grains of hydrocyanic acid, or rather more than 2 per cent (Dr. Clark).

Sulphocyanide of potassium; K , Cy S_2 ; 1222.2 or 97.92.—Sulphocyanogen is a salt-radical consisting of two of sulphur and one of cyanogen, which is formed on fusing the ferrocyanides with sulphur. To obtain it in combination with potassium, the ferrocyanide of potassium, made anhydrous by heat and reduced to a fine powder, is mixed with an equal weight of flowers of sulphur, in a common cast iron pot (pitch pot), and kept in a state of fusion for half an hour at a temperature inferior to that at which the sulphur would boil and bubbles of gas escape through the melted mass. No cyanogen is evolved or decomposed, and the residuary matter is a mixture of sulphocyanide of potassium and protosulphocyanide of iron, with the excess of sulphur. Both sulphocyanides dissolve in water, and give a solution which is colourless at first, but soon becomes red from oxidation of the sulphocyanide of iron. To get rid of the iron, carbonate of potash is added to the boiling solution, so long as a precipitate of carbonate of iron falls, and the liquid

is afterwards filtered. This solution gives crystals of sulphocyanide of potassium, when evaporated, which may be freed from any adhering carbonate of potash, by dissolving them in alcohol. The salt crystallizes in long white striated prisms, which are anhydrous, and resemble nitrate of potash in their appearance and taste. They deliquesce in a damp atmosphere, and are very soluble in hot alcohol, from which the salt crystallizes on cooling. The sulphocyanide of potassium communicates a blood red colour to solutions of salts of peroxide of iron, and is consequently employed as a test of that metal in its higher state of oxidation. The red solution is made perfectly colourless by a moderate dilution with water, when the iron is not present in excess. The sulphocyanide of potassium has been detected in the saliva of man and the sheep.

SALTS OF POTASH.

Carbonate of potash ; KO, CO_2 ; 866.3 or 69.42.—This useful salt is principally obtained from the ashes of plants. Potash is always contained in a state of combination in clay and other minerals which form the earthy part of soil, and appears to be a constituent of soil essential to vegetation. The alkali is appropriated by plants, and is found in their sap combined with vegetable acids, particularly with oxalic and tartaric acids ; also with silicic and sulphuric acids, and as chloride of potassium. When the plants are dried and burned, the salts of the vegetable acids are destroyed, and leave carbonate of potash ; shrubs yielding three, and herbs five times as much saline matter as trees ; and the branches of trees being more productive than their trunks, a distribution which may depend upon the potash existing chiefly in the sap. The whole ashes from wood seldom exceed 1 per cent of its weight, of which 1-6th may be saline matter. The solution evaporated to dryness yields *Potashes*, and these partially purified and ignited form *Pearlash*. The carbonate is mixed in the latter with about 20 per cent of foreign salts, principally sulphate of potash and chloride of potassium. The carbonate of potash is obtained in a state of greater purity by dissolving pearlash in an equal weight of water, then separating the solution from undissolved salts, and evaporating it to dryness.

Carbonate of potash is prepared of greater purity for chemical

purposes by igniting bitartrate of potash, or better by burning together 2 parts of that salt and 1 of nitre. In the latter process the carbon and hydrogen of the tartaric acid are destroyed by the oxygen of the nitric acid, and carbonate of potash remains mixed with charcoal, from which it may be separated by solution and filtration.

Carbonate of potash has an acrid, alkaline taste, but is not caustic. It gives a green colour to the blue infusion of cabbage. This salt is highly deliquescent, and soluble in less than an equal weight of water at 60° . It may be crystallized with two equivalents of water. Added to solutions of salts of lime, lead, &c., it throws down insoluble carbonates. It is more frequently used than the caustic alkali, to neutralise acids and to form the salts of potash.

Bicarbonate of potash; $\text{HO}, \text{CO}_2 + \text{KO}, \text{CO}_2$; 1255.3 or 100.61.—Formed by transmitting a stream of carbonic acid gas through a saturated cold solution of the neutral carbonate. It is soluble in four times its weight of water at 60° , and in less water at 212° . The solution has an alkaline taste and reaction, but is not acrid; it does not throw down magnesia from its soluble salts; it loses carbonic acid when evaporated at all temperatures, and becomes neutral carbonate. The salt contains one proportion of water, which is essential to it, and crystallizes well in prisms of eight sides, having dihedral summits. The existence of a sesquicarbonate of potash is doubtful.

Sulphate of potash; KO, SO_3 ; 1091.1 or 87.43. This salt precipitates when oil of vitriol is added drop by drop to a concentrated solution of potash. It is generally prepared by neutralising the residue, composed of bisulphate of potash, of the nitric acid process, (page 292), and crystallizes in double pyramids of six faces, or in oblique four-sided prisms. The crystals are anhydrous, unalterable in air, and they decrepitate strongly when heated; their density is 2.400. The sulphate is one of the least soluble of the neutral salts of potash; 100 parts of water dissolve 8.36 parts of this salt at 32° , and 0.99666 parts more for each degree above that point.

Hydrated bisulphate of potash, or Sulphate of water and potash; $\text{HO}, \text{SO}_3 + \text{KO}, \text{SO}_3$; 1704.7 or 136.59.—The fusible salt remaining when nitrate of potash is decomposed in a retort by two equivalents of oil of vitriol. Below 386.6° (197° cent.), it is a white crystalline mass. This salt is very soluble in water, but

is partially decomposed by that liquid, and deposits sulphate of potash. It crystallizes from a strong solution in rhombohedral crystals, of which the form is identical with one of the forms of sulphur. But this salt is dimorphous and crystallizes from a state of fusion by heat in large crystals, which have the form of felspar (Mitscherlich.) It was the only bisulphate of potash known before the unexpected discovery of another salt described below. Its density is 2.163. The excess of acid in this salt acts upon metals and alkaline bases, very much as if it were free.

Hydrated sesquisulphate of potash ; $\text{HO}, \text{SO}_3 + 2 (\text{KO}, \text{SO}_3)$.—A salt in prismatic needles discovered by Mr. Phillips, and which has also accidentally occurred since to M. Jacquelin. It is decomposed by water; the circumstances necessary for its formation are unknown.

Anhydrous bisulphate of potash ; $\text{KO} + 2\text{SO}_3$; 1592.2 or 127.59.—It appears, by M. Jacquelin's researches*, that this salt almost uniformly presents itself when sulphate of potash, and not less than one and a half equivalents of oil of vitriol are dissolved together in distilled water, and the solution evaporated. It crystallizes in prismatic needles, of which the density is 2.277, and point of fusion 410° (210° cent.) Left in their mother liquor, these crystals gradually disappear, and in their place, large rhombohedral crystals of the hydrated bisulphate are formed. The anhydrous salt may be dissolved and crystallized again from a quantity of hot water, not more than sufficient for its solution, but is decomposed by a larger quantity of water. This sulphate is analogous to the bichromate of potash; the constitution of these anomalous salts has already been made the subject of remark (page 328).

Sulphate of potash combines with *hydrated nitric and phosphoric acids*, as well as with hydrated sulphuric acid. On dissolving the neutral salt in nitric acid, a little nitre and hydrated bisulphate of potash are formed, with a large quantity of a salt in oblique prisms, of which the formula is $\text{HO}, \text{NO}_5 + 2 (\text{KO}, \text{SO}_3)$. This last salt fuses at 302° (150° cent.); its density is 2.38 (Jacquelin). The compound with phosphoric acid is formed by dissolving sulphate of potash in a syrupy solution of that acid, and crystallizes in oblique prisms of six sides, which fuse

* An. de Ch. et de Ph. t. 70, p. 311.

at 464° (240° cent.), and of which the density is 2.296 (Jacquelin.) Its formula is $3\text{HO}, \text{PO}_5 + 2\text{KO}, \text{SO}_3$. It will be observed that both these compounds agree with Mr. Phillips's sesquisulphate, in having two of sulphate of potash to one of hydrated acid.

Nitrate of potash, Nitre, Saltpetre; KO, NO_5 ; 1266.9 or 101.53.—Nitric acid is formed in the decomposition of animal matters containing nitrogen, when they are exposed to air, and are in contact with alkaline substances. It appears to be largely produced in this way in the soil of certain districts of India, from which nitrate of potash is obtained by lixiviation. Nitrous soils always contain much carbonate of lime, the debris of tertiary calcareous rocks, in which the oxygen and nitrogen of the air unite, according to some, assisted by the porous structure of the rock, and under the influence of an alkaline base, so as to generate nitric acid without the intervention of animal matter. But this conjecture is not founded upon experiment; nor is it a necessary hypothesis, since nitrifiable rocks are never entirely destitute of organic matter. Nitrate of potash is also prepared in some countries of Europe, by imitating the natural process, in artificial nitre-beds, wherein nitrate of lime is formed, and afterwards converted into nitrate of potash by the addition of wood-ashes to the lixivium*.

Nitrate of potash generally crystallizes in long striated six-sided prisms, is anhydrous, unalterable in the air, fusible into a limpid liquid by a heat under redness, in which condition it is cast in moulds, and forms *sal prunelle*. Its density is 1.933 (Dr. Watson). According to Gay-Lussac 100 parts of water dissolve 13.3 parts of this salt at 32° , 29 parts at 64.4° , 74.6 parts at 96.8° , and 236 parts at 206.6° . The taste of the solution is cooling and peculiar; it has considerable antiseptic properties. Nitre is insoluble in absolute alcohol.

* The latest writer upon nitrification is Professor Kuhlman, whose observations and original experiments are valuable, but do not lead to any general theory of the process. He did not succeed in causing oxygen and nitrogen gases to combine, by means of spongy platinum, but he found that, under the influence of that substance, (1°) all vaporisable compounds of nitrogen including ammonia, mixed with air, with oxygen, or with an oxidating gas, change into nitric acid or peroxide of nitrogen; and (2°) that all the vaporisable compounds of nitrogen, including nitric acid, mixed with hydrogen or a hydrogenous gas, give rise to ammonia.—(Memoirs of the Academy of Sciences of Lille, 1838, and Liebig's Annalen, Vol. 29, p. 272, 1839.)

From the large quantity of oxygen which nitre contains, and the facility with which it imparts that element to combustibles at a red heat, it is much employed in making gunpowder and other deflagrating mixtures. An intimate mixture of nitre in fine powder with 1-3rd of its weight of wood charcoal, when touched by a body in ignition, burns with great brilliancy, but without explosion. A mixture of 3 parts of nitre, 2 of dry carbonate of potash, and 1 of sulphur, forms *pulvis fulminans*, which heated gently till it enters into fusion, inflames suddenly, and explodes with a deafening report. The violence of the explosion is caused by the reaction between the sulphur and nitre being instantaneous, from their fusion and perfect intermixture, and the consequent sudden formation of much nitrogen gas from the decomposition of nitric acid. Gunpowder contains both sulphur and charcoal, of which the former serves the purpose of accelerating the process of deflagration and supplying heat, while the latter supplies much of the gas, to the formation of which the available force of the explosion is due. Gunpowder yields about 300 times its volume of gas, measured when cold; but its explosive force is greater than this indicates, from the high temperature of the gas, and not less than 1000 atmospheres. The ordinary proportions of gunpowder approach very nearly 1 eq. of nitre, 1 of sulphur, and 3 of carbon, as will be seen by the following comparison:—

COMPOSITION OF GUNPOWDER.

	Theoretical Mixture.	English.	Prussian.
Sulphur	. . 11.9	. . 12.5	. . 11.5
Charcoal	. . 13.5	. . 12.5	. . 13.5
Nitre	. . . 74.6	. . . 75.	. . . 75.
	<hr/> 100.	<hr/> 100.	<hr/> 100.

By the combustion of the mixture, carbonic acid and nitrogen gases are formed, with a solid residue of protosulphuret of potassium. Thus:—

DEFLAGRATION OF GUNPOWDER.

Before Decomposition.		After Decomposition.
3 Carbon.	3 Carbon.	3 Carbonic acid.
Nitrate of Potash.	{ 6 Oxygen.	Nitrogen.
	{ Nitrogen.	
	{ Potassium.	
Sulphur.	Sulphur.	Sulphuret of potassium.

A portion of the potash is always converted into sulphate of potash, which must interfere with the exactness of this decomposition. Blasting powder is composed of 20 sulphur, 15 charcoal, and 65 nitre; the proportion of sulphur being increased, by which a more powerfully explosive mixture is obtained, but which is not suitable for fire-arms, as they are injured by an excess of sulphur. The most inflammable charcoal is employed in making gunpowder; which is obtained by calcining branches of about 3-4ths of an inch in diameter, in an iron retort, for a considerable time, at a heat scarcely amounting to redness, and which has a brown colour without lustre. The granulation of gunpowder increases its explosive force. A charge is thus made sufficiently porous to allow flame to penetrate it, and to kindle every grain composing it at the same time. But still the discharge of gunpowder is not absolutely instantaneous; and it is remarkable that other explosive compounds which burn more rapidly than gunpowder, such as fulminating mercury, are not adapted for the movement of projectiles. Their action in exploding is violent but local; if substituted for gunpowder in charging ordinary fire-arms, they would shatter them to pieces, and not project the ball. It is a common practise to mix with the charge of blasting powder, used in mining, several times its bulk of sawdust, which renders the combustion of the powder still slower, but productive of a sustained effort, most effectual in moving large masses.

Chlorate of potash; KO, ClO_5 ; 1532.6 or 122.81.—This salt is the result of a reaction between chlorine and potash, which has already been explained (page 369.) In the preparation of chlorate of potash a strong solution of two or three pounds of carbonate of potash is made, and chlorine passed through it. The gas is conducted into the liquid by a pretty wide tube, or better by a tube terminated by a funnel, to prevent its being choked by the solid salt which is formed. A stage in the process can be observed, before the liquid has discharged much carbonic acid, when bicarbonate, chlorate, and hypochlorite of potash exist together in solution, and a considerable quantity of chloride of potassium is deposited. The latter salt is removed, and the current of chlorine continued till the liquid, which is often red from hypermanganic acid, becomes colourless or yellow, and ceases to absorb the gas. A considerable quantity of chlorate of potash is deposited in tabular shining crystals

which are purified by solution and a second crystallization, and more of the same salt is obtained from the liquid evaporated and set aside to crystallize; the separation of the chlorate from chloride of potassium depending upon the solubility at a low temperature of the former salt being greatly less than that of the latter. When chlorate of potash is prepared upon a still smaller scale, caustic potash may be substituted in the preceding process for carbonate. The solution, concentrated by heat, affords crystals of chlorate of potash upon cooling.

Chloride of lime, after it has lost the greater part of its bleaching power by keeping, a condition in which it is occasionally met with in commerce, contains chlorate of lime, and is available in the preparation of chlorate of potash. The solution of the lime salt is boiled for some time, to complete its change into chlorate and chloride; and then is partially decomposed by means of carbonate of potash, or evaporated with an admixture of chloride of potassium, when chlorate of potash crystallizes out, and chloride of calcium remains in solution (Löwig.)

This salt is anhydrous. It appears in flat crystals, of a pearly lustre, of which the forms, according to Brooke, belong to the oblique prismatic system. Its density is 1.989 (Hassénfratz). It has a cooling disagreeable taste, like that of nitre. According to Gay-Lussac, 100 parts of water dissolve $3\frac{1}{2}$ parts of chlorate of potash at 32° , 6 at 59° , 12 at 95° , 19 at 120.2° , and 60 at 219.2° , the point of ebullition of a saturated solution. This salt fuses readily in a glass retort or tube, enters into ebullition, and discharges oxygen below a red heat. At a certain period in the decomposition, when the mass becomes thick, a quantity of hyperchlorate of potash is formed, but ultimately chloride of potassium is the sole residue.

Chlorate of potash deflagrates with combustibles more violently than the nitrate. A grain or two of it rubbed in a warm mortar, with an equal quantity of sulphur, occasions smart explosions, with the formation of sulphurous acid gas. Inclosed with a little phosphorus, in paper, and struck by a hammer, it produces a powerful explosion; but this experiment may be attended with danger to the operator from the projection of the flaming phosphorus. A mixture which, when dry, inflames by percussion, and which is applied to lucifer matches, is composed of this salt, sulphur and charcoal. One of the simplest receipts for this percussion powder consists in washing out

the nitre from 10 parts of ordinary gunpowder, with water, and mixing the residue intimately, while still humid, with $5\frac{1}{4}$ parts of chlorate of potash in an extremely fine powder. This mixture is highly inflammable when dry, and dangerous to preserve in that state.

Hyperchlorate of potash; KO, ClO_7 ; 1732.6 or 138.83.—Processes for preparing this salt have already been described under hyperchloric acid (page 370). It is also formed in a strong solution of chlorate of potash contained in the decomposing cell of a voltaic battery, this salt being deposited in small crystals upon the zincoïd, and no oxygen liberated there. It requires 55 parts of water to dissolve it at 59° , but is largely soluble in boiling water. It crystallizes in octohedrons with a square base, which are generally small; they are anhydrous. It deflagrates less strongly with combustibles than the chlorate; loses oxygen at 400° , and is completely decomposed at a red heat, chloride of potassium being left.

Iodate of potash; KO, IO_7 ; 2669.4 or 213.92.—This salt may be formed by neutralising the chloride of iodine with carbonate of potash, instead of carbonate of soda (page 390). It gives small anhydrous crystals which fuse by heat, and lose all their oxygen. Iodic acid likewise forms a biniodate and a teriodate of potash, according to Serullas*. The *biniodate* is obtained by adding an additional proportion of iodic acid to a solution of neutral iodate saturated at a high temperature; it contains an equivalent of water, but may be made anhydrous by a strong heat, according to my own observations. It occurs in prisms with dihedral summits, and requires 75 parts of water at 59° to dissolve it. The *teriodate* is obtained on mixing a strong acid, such as nitric, hydrochloric, or sulphuric, with a hot saturated solution of the neutral iodate, and allowing it to cool slowly. It crystallizes in rhombohedrons, and requires 25 parts of water to dissolve it.

Serullas has observed that the biniodate of potash has a great disposition to form double salts. A compound with *chloride of potassium*, to which he assigned the formula $\text{K Cl} + \text{KO}, \text{I}_2\text{O}_{10}$, is obtained on adding a little hydrochloric acid to a solution of iodate of potash, and allowing the solution to evaporate spontaneously. This salt crystallizes well, but afterwards loses

* Ann. de Ch. et de Phys. t. 43.

its transparency in the air. It is decomposed by water, and cannot be formed by uniting its constituent salts. Another compound contains bisulphate of potash; KO , $\text{S}_2\text{O}_6 + \text{KO}$, I_2O_{10} . This salt is obtained from the mother liquor which remains in the preparation of the teriodate of potash, after treatment with sulphuric acid. When that liquor is evaporated by heat, this salt is deposited in transparent regular crystals. Like the preceding salt it is decomposed by water, and cannot be formed directly. These two salts and the teriodate of potash, merit a re-examination, in reference to their containing water as a constituent.

SECTION II.

SODIUM.

Syn. NATRIUM. *Eq.* 291 or 23.31; Na.

Davy obtained this metal by the voltaic decomposition of soda, immediately after the discovery of potassium. An intimate mixture of charcoal and carbonate of soda is obtained by calcining acetate of soda, from which sodium is commonly prepared, according to the method described for potassium, and with greater facility, owing to the superior volatility of this metal.

Sodium is a white metal having the aspect of silver. Its density is 0.972, at 59° , according to Gay-Lussac and Thenard. This metal is so soft, at the usual temperature, that it may be cut with a knife, and yields to the pressure of the fingers; it is quite liquid at 194° . It oxidates spontaneously in the air, although not so quickly as potassium; and when heated nearly to redness takes fire and burns with a yellow flame. Thrown upon water, it oxidates with great vivacity, but without inflaming, evolving hydrogen gas, and forming an alkaline solution of soda. When a few drops only of water are applied to sodium, it easily becomes sufficiently hot to take fire.

As potassium is in some degree characteristic of the vegetable kingdom, so sodium is the alkaline metal of the animal kingdom, its salts being found in all animal fluids. Both of these elements occur in the mineral world; of the two, perhaps, potassium is most extensively diffused; felspar, the most common of minerals, containing 12 per cent. of potash, but

from the existence everywhere of a soluble compound of sodium, its chloride, the sources of that element are the more accessible, if not the most abundant.

The anhydrous protoxide of sodium and the peroxide are prepared in the same manner as the corresponding oxides of potassium, which they greatly resemble in properties. The composition of the peroxide of sodium, however, is different, being expressed by the formula $2\text{Na} + 3\text{O}$ (Thénard). It is supposed by M. Millon to be $\text{Na} + 2\text{O}$.

COMPOUNDS OF SODIUM.

Soda; Na O ; 391 or 31.31.—A solution of soda is obtained by decomposing the crystallized carbonate of soda, dissolved in 4 or 5 times its weight of water, by means of half its weight of hydrate of lime; the same points being attended to as in the preparation of potash. A preference is given to this alkali from its cheapness, for most manufacturing purposes, and in the laboratory it may generally be substituted for potash, where a caustic alkali is required. On the large scale it is prepared from *salts of soda*, a carbonate containing chloride of sodium and sulphate of soda. The solution of soda is purified from these salts by concentrating it considerably, upon which the foreign salts cease to be soluble in the liquid and precipitate (Mr. W. Blyth).

The following table, constructed by Dr. Dalton, exhibits the quantity of caustic soda in solutions of different densities:—

SOLUTION OF CAUSTIC SODA.

Density of the solution.	Alkali per cent.	Density of the solution.	Alkali per cent.
2.00 .	. 77.8	1.40 .	. 29.0
1.85 .	. 63.6	1.36 .	. 26.0
1.72 .	. 53.8	1.32 .	. 23.0
1.63 .	. 46.6	1.29 .	. 19.0
1.56 .	. 41.2	1.23 .	. 16.0
1.50 .	. 36.8	1.18 .	. 13.0
1.47 .	. 34.0	1.12 .	. 9.0
1.44 .	. 31.0	1.06 .	. 4.7

The solid hydrate of soda is obtained by evaporating a solution of soda, precisely in the same manner as the corresponding preparation of potash. It is soluble in all proportions in water and alcohol.

Soda is distinguished from potash and other bases by several

properties :—1st. All its salts are soluble in water, and it is therefore not precipitated by tartaric acid, chloride of platinum, or any other reagent. 2nd. With sulphuric acid it affords a salt which crystallizes in large efflorescent prisms, easily recognised as Glauber's salt. 3rd. Its salts communicate a rich yellow tint, to flame.

Sulphurets of sodium.—These compounds so closely resemble the sulphurets of potassium as not to require a particular description. The protosulphuret of sodium crystallizes from a strong solution in octohedrons. This salt contains water of crystallization; in contact with air it rapidly passes into caustic soda, and the hyposulphite of the same base.

Chloride of sodium, Sea salt, Common salt ; Na Cl ; 733.6 or 58.78.—Sodium takes fire in chlorine gas, and combining with that element, produces this salt. The chloride of sodium is also formed on neutralising hydrochloric acid, by soda or its carbonate, and is obtained thus in the greatest purity. Sea-water contains 2.7 per cent of chloride of sodium, which is the most considerable of its saline constituents (analysis of sea-water at page 266). Salt is obtained from that source in warm climates, as at St. Ubes, in Portugal, on the coast of the Mediterranean near Marseilles, and other places where spontaneous evaporation proceeds rapidly; the sea-water being retained in shallow basins or canals, on the surface of which a saline crust forms, with the progress of evaporation, which is broken and raked out. Sea-water is also evaporated artificially, by means of culm, or waste coal, as fuel, on some parts of the coast of Britain, but as much for the sake of the *bittern* as of the common salt it affords. The evaporation is not carried to dryness, but when the greater part of the chloride of sodium is deposited in crystals, the mother liquid, which forms the *bittern*, is drawn off; it is the source of much of the Epsom salt and other magnesian preparations of commerce. Other inexhaustible sources of common salt are the beds of sal-gem or rock salt, which occur in several geological formations posterior to the coal, as at Northwich in Cheshire, in Spain, Poland, and many other localities. These beds appear to have been formed by the evaporation of salt lakes without an outlet, in which the saline matter, continually supplied by rivers, had accumulated, till the water being saturated, a deposition of salt took place upon the bottom of the lake. The salt is some-

times sufficiently pure for its ordinary uses, as it is taken from these deposits, but more generally it is coloured brown from an admixture of clay, and requires to be purified by solution and filtration. Instead of sinking a shaft to the bed of rock salt, and mining it, the superior strata are often pierced by a bore of merely a few inches in diameter, by which water is admitted to the bed, and the brine formed drawn off by a pump and pipe of copper suspended in the same tubular opening.

Chloride of sodium crystallizes from solution in water in cubes, and sometimes from urine and liquids containing phosphates in the allied form of the regular octohedron. Its crystals are anhydrous, but decrepitate when heated, from the expansion of water confined between their plates. According to the experiments of Fuchs, pure chloride of sodium has exactly the same degree of solubility in hot and cold water, requiring 2.7 parts of water to dissolve it; or 100 parts of water dissolve 37 of salt at all temperatures. The composition of such a solution corresponds exactly with 1 eq. of salt to 18 eq. of water. Gay-Lussac makes the boiling point of a saturated solution 229.5° , but that temperature is too high (I believe,) for a solution of pure chloride of sodium. When a saturated solution is exposed to a low temperature, between 14° and 5° , the salt crystallizes in hexagonal tables, which have two sides larger than the others. Fuchs found these crystals to contain 6, and Mitscherlich 4 equivalents of water. If their temperature is allowed to rise above 14° , they undergo decomposition, and are converted into a congeries of minute cubes, from which water separates.

Pure chloride of sodium has an agreeable saline taste, deliquesces slightly in damp weather, and dissolves largely in rectified spirits, but is very slightly soluble in absolute alcohol. Its density is 2.557 (Mohs). It fuses at a bright red heat, and at a higher temperature rises in vapour. It is immediately decomposed by oil of vitriol, with the evolution of hydrochloric acid. Besides being used as a seasoning for food, chloride of sodium is employed in the preparation of the sulphate and carbonate of soda. When ignited in contact with clay containing oxide of iron, the sodium of this salt becomes soda, and unites with the silica of the clay, while the chlorine combines with iron, and is volatilised. On this decomposition is founded the mode of communicating the salt-glaze to pottery: a quantity of salt is thrown into the kiln, where it is converted into vapour by the

heat, and condensing upon the surface of the pottery causes its vitrification, which is attended with the formation of hydrochloric acid, and perchloride of iron.

The bromide and iodide of sodium crystallize in cubes, and resemble in properties the corresponding compounds of potassium. The other compounds of sodium are not of particular interest.

SALTS OF SODA.

Carbonate of soda; $\text{NaO}, \text{CO}_2 + 10\text{HO}$; 667.3 + 1125, or 53.47 + 90.—This useful salt is found nearly pure in commerce, in large crystals, which effloresce when exposed to air. These crystals contain 10 equivalents of water, and consist in 100 parts, of 21.81 soda, 15.43 carbonic acid, and 62.76 water. According to Dr. Thomson, they generally contain about $\frac{1}{2}$ per cent of sulphate of soda, as an accidental impurity. Their form appears to belong to the oblique prismatic system. Their density is 1.623; 100 parts of water dissolve 20.64 of the crystals at 58.25° , and more than an equal weight at the boiling temperature (Dr. Thomson). In warm weather the carbonate of soda sometimes crystallizes in another form of crystal, which is not efflorescent, and of which the proportion of water is variously stated by Mitscherlich and Thomson at 7 and 8 equivalents. A third hydrate was obtained by Mohs, on allowing a solution of carbonate of soda, saturated between 68° and 86° , to cool; which was found to contain 17.74 per cent. of water, a result somewhat exceeding 1 equivalent. On evaporating a solution of carbonate of soda at the boiling point, the salt precipitates in a powder, which contains nearly the same proportion of water.

This salt has a disagreeable alkaline taste. When heated it undergoes the watery fusion; its water is soon dissipated, and a white anhydrous salt remains, which again becomes liquid at a red heat, undergoing then the igneous fusion. A mixture of carbonates of potash and soda is more fusible than either salt separately.

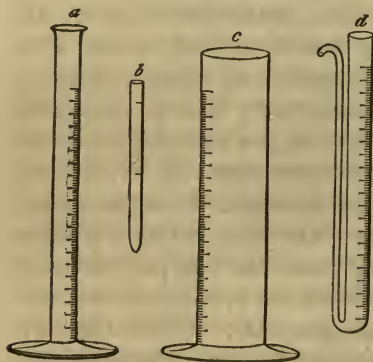
Carbonate of soda is prepared by a process which will be described immediately, under the head of sulphate of soda. Much of the carbonate of commerce is not crystallized, but simply evaporated to dryness, and is then known as *salts of soda*. In this form it always contains chloride of sodium, sul-

phate of soda, and often insoluble matter, and varies considerably in value. The soda in combination with carbonic acid only, is available in the application of the salt as an alkaline substance. The pure anhydrous carbonate of soda consists of 58.58 soda and 41.42 carbonic acid, but the best soda-salts of commerce rarely contain so much as 50 per cent. of available soda. The operation of ascertaining the proportion of alkali in these salts, and in other forms of the carbonate of soda, is a process of importance from its frequent occurrence, and interesting as a method of analysis of easy execution and applicable to a great variety of substances. I shall therefore describe minutely the mode of conducting it.

ALKALIMETRY.

The experiment is to find how many measures of a diluted acid are required to destroy the alkaline reaction of, and to neutralise 100 grains of a specimen of soda-salt. (1) The acid is measured in the alkalimeter, which is a straight glass tube, or

FIG. 47.



very narrow jar with a lip, about 5-8ths. of an inch in width, and 14 inches in height, mounted upon a foot, as *a* of figure 47, capable of containing at least 1000 grains of water. It is graduated into 100 parts, each of which holds ten grains of water. In the operation of dividing such an instrument it is more convenient to use measures of mercury than water; 135.68 grains of mercury, being

in bulk equal to 10 grains of water, 678.40 grains will be equal to 50 grains of water. A unit measure may be formed of a pipette, *b* in figure 47, made to hold the last quantity of mercury, into which the metal is poured, the opening at the point of the pipette being closed by the finger, and the height of the mercury in the tube marked by a scratch on the glass, made by a triangular file. The bulk of twice that quantity of mercury, or 100 water grain measures, may likewise be marked upon the tube. The former quantity of mercury is then de-

canted from the tube into the alkalimeter to be graduated, and a scratch made upon the latter at the mercury surface: this is 5 of the ten-grain water measures. Another measure is added and its height marked; and the same repeated till 20 measures of mercury in all have been added, which are 100 ten-grain water measures. The subdivision of each of these measures into 5 is best made by the eye, and is also marked on the alkalimeter. The divisions are lastly numbered, 0, 5, 10, &c., counting from above downwards, and terminating with 100 on the sole of the instrument. Several alkalimeters may be graduated at the same time, with little more trouble than one, the measured quantities of mercury being transferred from one to the others in succession. The French alkalimeter, *d* of figure 47, is a more convenient instrument to pour from, but it is too fragile for common use.

(2) To form the test acid, 4 ounces avoirdupois of oil of vitriol are diluted with 20 ounces of water; or larger quantities of acid and water are mixed in these proportions. About $\frac{3}{4}$ ths of an ounce of bicarbonate of soda is heated strongly by a lamp for a few minutes, to obtain pure carbonate of soda; of which 171 grains are immediately weighed; that quantity, or more properly 170.6 grains, containing 100 grains of soda. This portion of carbonate of soda is dissolved in 4 or 5 ounces of hot water; and the alkalimeter filled up to 0, with the dilute acid. The acid is poured gradually into the soda solution, till the action of the latter upon test-paper ceases to be alkaline, and becomes distinctly acid, and the measures of acid necessary to produce that change accurately observed. It may probably require about 90 measures. But it is convenient to have the acid exactly of the strength at which 100 measures of it saturate 100 grains of soda. A plain cylindrical jar *c*, of which the capacity is about a pint and a half is graduated into 100 parts, each containing 100 grain measures of water, or ten times as much as the divisions of the alkalimeter. The divisions of this jar, however, are numbered from the bottom upwards, as is usual in measures of capacity. This jar is filled up with the dilute acid to the extent of 90, or whatever number of the alkalimeter divisions of acid were found to neutralise 100 grains of soda; and *water* is added to make up the acid liquid to 100 measures. Such is the test acid, of which 100 alkalimeter measures neutralise, and are equivalent to 100 grains of soda; or 1 measure

of acid to 1 grain of soda. It is transferred to a stock bottle. The remainder of the original dilute acid is diluted with water to an equal extent, in the same instrument, and added to the bottle. The density of this acid is 1.0995 or 1.0998, which is sensibly the same as 1.1. By a curious coincidence, strong oil of vitriol diluted with 11 times its weight of water, gives this test acid exactly; but as oil of vitriol varies a little in strength, it is better to form the test acid in the manner described, than to trust to that mixture. Twenty-one measures of the test acid should neutralise 100 grains of cr. carbonate of soda; and 58.5 measures, 100 grains of pure anhydrous carbonate of soda.

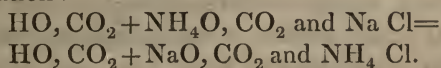
(3) In applying the test acid, it is poured from the alkali-meter, as before, upon 100 grains of the soda-salt to be tested, dissolved in two or three ounces of hot water. The salt contains so many grains of soda, as it requires measures of acid to neutralise it; and therefore so much alkali per cent. If the soda-salt is mixed with insoluble matter, its solution must be filtered before the test acid is added to it. In examining a soda-salt which blackens salts of lead, and contains both carbonate of soda and sulphuret of sodium, 100 grains are tested as above, and the whole alkali in both salts thus determined. A neutral solution of chloride of calcium is also added in excess to the solution of a second hundred grains, by which the carbonate of soda is converted into chloride of sodium, while carbonate of lime precipitates. The filtered liquid is still alkaline, and contains all the sulphuret of sodium; the quantity of soda corresponding with which is ascertained by means of the test acid. The difference between the quantities of alkali observed in the two experiments is the proportion of soda present, as carbonate.

Borax also may be analyzed by the same test acid, and will be found when pure to contain 16.37 per cent of soda. The carbonates of potash may also be examined by the same means, but the per centage of alkali must then be estimated higher than the measures of acid neutralised, in the proportion of the equivalent of soda to that of potash, which are to each other very nearly as 39 to 59. The test paper employed in alkalimetry must be delicate. It should be prepared on purpose, by dipping good letter-paper several times in a filtered infusion of litmus, and drying it after each immersion, till the paper is of a deep purple colour. A test paper prepared with cudbear in the same way answers still better, but the latter colouring matter is not

easily obtained of good quality. The operator must also make himself familiar with the difference between the slight reddening of his test paper, by carbonic acid, which is disengaged, and the unequivocal reddening produced by a strong acid, which last is the indication to guide him.

Bicarbonate of soda; $\text{HO}, \text{CO}_2 + \text{NaO}, \text{CO}_2$; 1056.2 or 84.64.—This salt is prepared by transmitting a stream of carbonic acid through a saturated solution of the neutral carbonate; it is then deposited as a farinaceous powder, but may be obtained in crystals from a weaker solution. It requires 13 times its weight of cold water to dissolve it. Although containing two equivalents of acid, this salt is alkaline to test paper, but its taste is much less unpleasant than the neutral carbonate, and indeed is scarcely perceived when combined with a little common salt. The proportion of alkali in bicarbonate of soda is 37.0 per cent, but the salt of commerce generally contains upwards of 40 per cent, owing to the presence of neutral carbonate in the state of protohydrate, which last salt may be separated by a small quantity of water.

The bicarbonate of soda is also obtained otherwise by an interesting reaction. Equal weights of common salt and carbonate of ammonia of the shops are taken; the former is dissolved in three times its weight of water, and the latter added in a state of fine powder to this solution, the whole stirred well together, and allowed to stand for some hours. The bicarbonate of oxide of ammonium present reacts upon chloride of sodium, producing the sparingly soluble bicarbonate of soda, which precipitates in crystalline grains and causes the liquid to become thick, and chloride of ammonium (sal ammoniac), which remains in solution:—



The solid bicarbonate of soda is separated from the liquid by pressure in a screw press; but retains a portion of chloride of sodium. Messrs. Hemming and Dyer, who first observed this reaction, have proposed to found upon it a process for obtaining carbonate of soda from common salt.

Sesquicarbonate of soda; $2\text{NaO} + 3\text{CO}_2 + 4\text{HO}$; 2061 or 163.15.—This salt presents itself occasionally in small prismatic crystals, but cannot be prepared at pleasure. It is unalterable in the air, but is decomposed in the dry state, I find, by a less degree of heat than the bicarbonate, notwithstanding its con-

taining a smaller excess of carbonic acid. The theoretical carbonate of water, supposed to resemble the carbonate of magnesia, will be $\text{HO}, \text{CO}_2, \text{HO} + 2\text{HO}$; which gives the salt in question, if the last 2HO are replaced by two proportions of protohydrated carbonate of soda. Substitutions of this character appear to be common, in the formation of double carbonates and oxalates. The bicarbonate of potash may be formed by the substitution of carbonate of potash for the first HO , in this carbonate of water, while the other 2HO disappear. This salt occurs native in several places, particularly on the banks of the lakes of soda in the province of Sukena, in Africa, whence it is exported under the name of *Trona*, in Egypt, Hungary, and in Mexico, and has the same proportion of water as the artificial salt.

Sulphate of soda, Glauber's salt; $\text{NaO}, \text{SO}_3 + 10\text{HO}$; 892.1. + 1125, or 71.48 + 90.—This salt occurs crystallized in nature, and also dissolved in mineral waters, and is formed on neutralising carbonate of soda by sulphuric acid. But it is more generally prepared by decomposing common salt with sulphuric acid, as in the process for hydrochloric acid (page 362.) The sulphate of soda crystallizes readily in long prisms, of which the sides are often channeled, which have a cooling and bitter taste, and contain 55.76 per cent of water, or 10 equivalents; in which they fuse by a slight elevation of temperature, and which they lose by efflorescence in dry air. At 32° , 100 parts of water dissolve 5.02 parts of anhydrous sulphate of soda, 50.65 parts at 91° , which is the temperature of maximum solubility of this salt, and 42.65 parts at the boiling temperature. In a supersaturated solution of this salt (page 263), crystals are sometimes slowly deposited, which are different in form and harder than, Glauber's salt; they contain 8 equivalents of water. A saturated solution of sulphate of soda, kept at a temperature between 91° and 104° , affords octohedral crystals with a rhombic base, which are anhydrous. They are isomorphous with the hypermanganate of barytes.* Their density is 2.642. The anhydrous salt fuses at a bright red heat, without loss of acid. Sulphate of soda was at one time the saline aperient in common

* Dr. Clark considers this isomorphism not fortuitous, and founds on it an interesting speculation respecting the constitution of soda. It leads him to double the atomic weight of sodium, or to estimate it at 582, which he represents by So , and to make soda a peroxide, " So " O_2 , which like other peroxides unites with as many proportions of acid as it contains of

use, but is now superseded by sulphate of magnesia. It is still, however, combined with the tartrate of potash and soda, in Seidlitz powders.

PREPARATION OF CARBONATE OF SODA FROM THE SULPHATE.

The sulphate of soda is chiefly formed, as a step in the process of preparing soda from common salt. The same manufacture requires large quantities of sulphuric acid, not less than 12,000 tons of sulphur being annually converted into that acid in England; and by means of the acid, 50,000 tons of salt converted into sulphate of soda. From the last, upwards of 50,000 tons of *soda ash*, and 20,000 tons of crystallized carbonate of soda were manufactured, in 1838; and the manufacture is greatly on the increase.*

A reverberatory furnace is employed in soda-making and various other chemical manufactures, to afford the means of exposing a considerable quantity of materials to a strong heat, of which a perpendicular and a horizontal section are given in

FIG. 48.

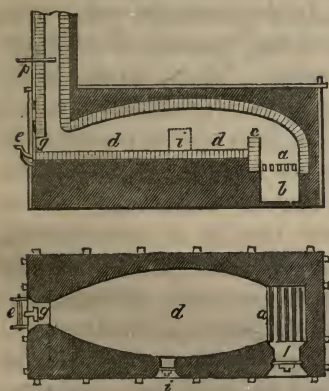


figure 48. It consists of a fire-place *a*, in which the fuel is burned, of which *b* is the ash-pit, with a horizontal flue expanded into a small chamber or oven *d d*, which is raised to a strong red heat, by the reverberation on its walls of the flame, or heated air from the fire, on its passage to the chimney. The matters to be heated are placed upon the floor of this chamber. It has an opening *i* in the side, for the introduction of materials, and another opening *g* at the end most

oxygen, or with two. The relation between the two salts is thus brought out:—

Hypermanganate of barytes is, $\text{Ba O} + \text{Mn}_2 \text{O}_7$

Or, on the binary theory of salts, $\text{Ba} + \text{Mn}_2 \text{O}_8$.

Two atoms of sulphate of soda, on the same theory, are $\text{Na}_2 + \text{S}_2 \text{O}_8$;

Or, 2Na being really “So,” “So” + $\text{S}_2 \text{O}_8$.

It will be observed that, as represented by the second and fourth formulæ, hypermanganate of barytes and sulphate of soda have a similar atomic constitution; they should therefore be isomorphous.—(Records of General Science, Vol. IV., page 45.)

* Information supplied by Mr. Muspratt of Liverpool.

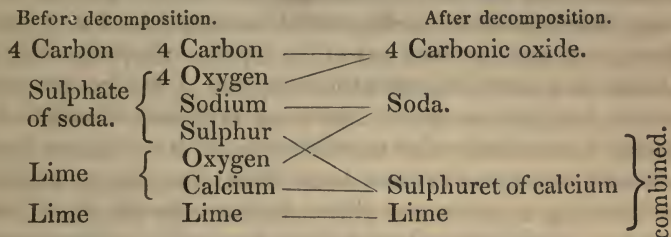
distant from the fire; the chimney is provided with a damper *p*, by which the draught is regulated.

(1) The sulphate of soda is prepared by throwing 600 pounds of common salt into the chamber of the furnace, already well heated, and running down upon it from an opening in the roof, an equal weight of sulphuric acid of density 1.600, in a moderate stream. Hydrochloric acid is disengaged and carried up the chimney, and the conversion of the salt into sulphate of soda is completed in four hours. (2) The sulphate thus prepared is reduced to powder and mixed with an equal weight of ground chalk, and half its weight of small coal ground and sifted. This mixture is introduced into a very hot reverberatory furnace, about two hundred weight at a time. It is frequently stirred until it is uniformly heated. In about an hour it fuses, is then well stirred for about five minutes, and drawn out with a rake into a cast iron trough, in which it is allowed to cool and solidify. This is called ball soda or British barilla, and contains about 22 per cent of alkali. (3) To separate the salts from insoluble matter, the cake of ball soda, when cold, is broken up, put into vats, and covered by warm water. In six hours the solution is drawn off from below, and the washing repeated about eight times, to extract all the soluble matter. These liquors being mixed together are boiled down to dryness, and afford a salt which is principally carbonate of soda, with a little caustic soda and sulphuret of sodium. (4) For the purpose of getting rid of the sulphur, the salt is mixed with one-fourth of its bulk of sawdust, and exposed to a low red heat in a reverberatory furnace for about 4 hours, which converts the caustic soda into carbonate, while the sulphur also is carried off. This product contains about 50 per cent of alkali, and forms the soda-salt of best quality. (5) If the crystallized carbonate is required, the last salt is dissolved in water, allowed to settle, and the clear liquid boiled down until a pellicle appears on its surface. The solution is then run into shallow boxes of cast iron to crystallize, in a cool place; and after standing for a week the mother liquor is drawn off, the crystals drained, and broken up for the market. (6) The mother liquor, which contains the foreign salts, is evaporated to dryness for a soda salt, which serves for soap or glass making, and contains about 30 per cent. of alkali.

The most essential part of this process is the fusion of sulphate of soda with coal and carbonate of lime; by the first, the sulphate is converted into sulphuret of sodium (page 448), and

by the second the sulphuret of sodium is converted into carbonate of soda; and, if desirable, these changes may be effected separately, by calcining the sulphate with coal and carbonate of lime in succession. The lime becomes at the same time sulphuret of calcium, a compound which would destroy the carbonate of soda, if dissolved along with that salt, in the subsequent lixiviation of the ball soda. But although possessed of a certain degree of solubility, the sulphuret of calcium does not dissolve in the experiment, from being in combination with lime, as an oxisulphuret of calcium. Hence an excess of lime is necessary in the process. The application, however, of very hot water to the ball soda is to be avoided, as the oxisulphuret is decomposed at a high temperature, and sulphuret of calcium dissolved out. The following diagram will represent the chemical changes in this process, supposing for simplicity that charcoal is employed instead of coal, and lime instead of its carbonate; the numbers denoting equivalents :—

REACTION IN THE SODA PROCESS.



The soda derives carbonic acid from the carbonate of lime or from the fire, and is therefore obtained principally as carbonate.

The insoluble oxisulphuret of calcium of this process is known as soda-waste. It has hitherto been not merely valueless but troublesome to the manufacturer. But the attempt is at present made to turn it to account as a source of sulphur. Means are taken to condense the hydrochloric acid, formerly sent up the chimney, and this acid is applied to the soda-waste, from which it disengages sulphuretted hydrogen, and carbonic acid. But hydrochloric acid is not produced, in the soda process, in adequate quantity for this application of it, and carbonic acid evolved with sulphuretted hydrogen might interfere with the combustion of the latter. These difficulties, however, are in a great degree removed by the discovery of Mr. Gossage, that

sulphuret of calcium, when moistened, is decomposed easily and completely by a single equivalent of carbonic acid. Hence the application of hydrochloric acid to the waste may be made, with the evolution of nothing but sulphuretted hydrogen; and the deficiency in the quantity of hydrochloric acid may be made up by a supply of carbonic acid, to be applied to the waste, from any other source. The sulphuretted hydrogen is burned, instead of sulphur, in the leaden chamber, to reproduce sulphuric acid.

Many changes have been proposed upon the soda process. Sulphate of iron, produced by the oxidation of iron-pyrites, is a cheap salt, and may be applied to convert chloride of sodium into sulphate of soda,—(1) by igniting a mixture of these salts in a reverberatory furnace, when sulphate of soda, peroxide of iron and volatile perchloride of iron are produced: (2) by dissolving the salts together in water, and allowing the solution to fall to a low temperature, when sulphate of soda crystallizes, and chloride of iron remains in solution (Mr. Phillips); or (3) by concentrating the last solution at the boiling point, when the same decomposition occurs, anhydrous sulphate of soda precipitates, and may be raked out of the liquor. Sulphate of magnesia has also been substituted for sulphate of iron, in these three modes of application. It has been proposed, instead of furnacing the sulphate of soda, to decompose it by caustic barytes. Chloride of sodium has also been decomposed by moistening it, and rubbing it in a mortar with 4 or 6 times its weight of litharge, when an oxichloride of lead is formed, and caustic soda liberated. The decomposition of chloride of sodium by the carbonate of ammonia, with formation of bicarbonate of soda, has already been noticed (page 469). It appears, however, that the soda-process first described, which was invented towards the end of last century by Leblanc, is still generally preferred to all others.

The old sources of carbonate of soda, namely *barilla*, or the ashes of the salsola soda, which is cultivated on the coasts of the Mediterranean, and *kelp*, the ashes of sea-weeds, have ceased to be of importance, at least, in England. Barilla contains about 18, and kelp about 2 per cent of alkali.

Bisulphate of soda; $\text{HO}, \text{SO}_3 + \text{NaO}, \text{SO}_3$; 1505.7 or 120.64. This salt is obtained in large crystals on adding an equivalent of oil of vitriol to sulphate of soda, and evaporating the solution till it attains the degree of concentration necessary for crystalliza-

tion. If half an equivalent only of oil of vitriol is added, a *sesquisulphate of soda* is obtained in fine crystals, according to Mitscherlich.

Nitrate of soda; NaO, NO_5 ; 1067.9 or 85.57.—This salt crystallizes in the rhomboidal form of calc-spar. It is soluble in twice its weight of cold water, and has a tendency to deliquesce in damp air. It burns much slower with combustibles than nitrate of potash, and cannot therefore be substituted for that salt in the manufacture of gunpowder. It is now generally had recourse to, as the source of nitric acid. Nitrate of soda is found abundantly in the soil of some parts of India; and at Atacama in Peru, it covers large districts, from which it is exported in considerable quantity.

Chlorate of soda (NaO, ClO_5) is formed by mixing strong solutions of bitartrate of soda and chlorate of potash, when the bitartrate of potash precipitates, and the chlorate of soda remains in solution. It crystallizes in fine tetrahedrons, and is considerably more soluble than chlorate of potash.

Phosphates of soda.—There are three crystallizable phosphates of soda belonging to the tribasic class, which I shall describe under their old names.

Phosphate of soda; $\text{HO}, 2\text{NaO}, \text{PO}_5 + 24\text{HO}$; 4486.6 or 359.15.—This is the salt known in pharmacy as phosphate of soda, and formed by neutralising phosphoric acid from burnt bones (page 346) with carbonate of soda. It crystallizes in oblique rhombic prisms, which are efflorescent, and essentially alkaline. The taste of phosphate of soda is cooling and saline, and less disagreeable than sulphate of magnesia, for which it may be substituted as an aperient. It dissolves in 4 times its weight of cold water, and fuses in its water of crystallization, when moderately heated. When evaporated above 90° , this salt crystallizes in another form with 14 instead of 24 atoms of water (Clark). It is deprived of half its alkali by hydrochloric acid, but not by acetic acid.

Subphosphate of soda; $3\text{NaO}, \text{PO}_5 + 24\text{HO}$; 4764.5 or 381.78.—Formed when an excess of caustic soda is added to the preceding salt. It crystallizes in slender six-sided prisms with flat terminations, which are unalterable in air; but the solution of this salt rapidly absorbs carbonic acid, and is deprived of one-third of its alkali by the weakest acids. The crystals dissolve in 5 times their weight of water at 60° , and undergo the watery

fusion at 170° . This salt continues tribasic after being exposed to a red heat.

Biphosphate of soda ; $2\text{HO}, \text{NaO}, \text{PO}_5 + 2\text{HO}$; 1733.1 or 138.88.—Obtained by adding tribasic phosphate of water to phosphate of soda, till the latter ceases to produce a precipitate with chloride of barium. The solution affords crystals, in cold weather, of which the ordinary form is a right rhombic prism, having its larger angle of $93^{\circ} 54'$. But this salt is dimorphous, occurring in another right rhombic prism, of which the smaller angle is $78^{\circ} 30'$, terminated by pyramidal planes, isomorphous with binarsenate of soda. The biphosphate of soda is very soluble, and has a distinct acid reaction. Like all the other soluble tribasic phosphates, it gives a yellow precipitate with nitrate of silver, which is tribasic phosphate of silver.

Phosphate of soda and ammonia, Microcosmic salt ; $\text{HO}, \text{NH}_4\text{O}, \text{NaO}, \text{PO}_5 + 8\text{HO}$.—This salt is obtained by heating together 6 or 7 parts of crystallized phosphate of soda, and 2 parts of water, till the whole is liquid, and then adding 1 part of powdered sal ammoniac. Chloride of sodium separates, and the solution, filtered and concentrated, affords the phosphate in prismatic crystals. It is purified by a second crystallization. This salt occurs in large quantity in urine. It is much employed as a flux in blow-pipe experiments. By a slight heat it loses 8HO , by a stronger heat it is deprived of its remaining water and ammonia, and converted into metaphosphate of soda, which is a very fusible salt. It will be observed that the three atoms of base in this phosphate are all different, namely water, oxide of ammonium, and soda ; of which the two last belong to the same natural family. This salt, I believe, proved the key to the constitution of the bibasic and tribasic organic acids, by supplying the canon, founded upon it by myself, that bases of the same family may exist together in the salts of such acids, but not in ordinary double salts ; which was happily applied to elucidate the salts of the acids in question by MM. Liebig and Dumas. No phosphate exists, corresponding with microcosmic salt, but containing potash instead of oxide of ammonium ; the phosphate of soda, with 14HO , has been mistaken for such a salt.

Pyrophosphate of soda ; $2\text{NaO}, \text{PO}_5 + 10\text{HO}$; 1674.1 + 1125, or 134.15 + 90.—Procured by heating the phosphate of soda to redness, when it loses its basic water as well as its water of crystallization. The residual mass dissolved in water affords a salt,

which is less soluble than the original phosphate, and crystallizes in prismatic crystals, which are permanent in air, and contain ten atoms of water. Its solution is essentially alkaline. This salt is precipitated white, by nitrate of silver. It is to be remarked that insoluble pyrophosphates, including pyrophosphate of silver, are soluble to a considerable degree in the solution of pyrophosphate of soda. The pyrophosphates of potash and of ammonia can exist in solution, but pass into tribasic salts when they crystallize.

A *bipyrophosphate of soda* ($\text{HO}, \text{NaO}, \text{PO}_5$) exists, obtained by the application of a graduated heat to the biphosphate of soda, but it does not crystallize. Its solution has an acid reaction.

Metaphosphate of soda; NaO, PO_5 ; 1283.2 or 102.82.—The three phosphates last described, all contain but one equivalent of fixed base, and afford the metaphosphate of soda, when heated to redness; microcosmic salt being readily procured, may be recommended for that purpose. The metaphosphate of soda fuses at a heat, which does not exceed low redness, and on cooling forms a transparent glass, which is deliquescent in damp air, and very soluble in water, but insoluble in alcohol; its solution has a feeble acid reaction, which can be negatived by the addition of 4 per cent of carbonate of soda. When evaporated, this solution does not give crystals, but dries into a transparent pellicle, like gum, which retains at the temperature of the air somewhat more than a single equivalent of water. Added to neutral, and not very dilute solutions of earthy and metallic salts, metaphosphate of soda throws down insoluble hydrated metaphosphates, of which the physical condition is remarkable. They are all soft solids, or semifluid bodies; the metaphosphate of lime having the degree of fluidity of Venice turpentine. An account has already been given of the singular change, at a particular temperature, of hydrated metaphosphate of soda into bipyrophosphate of soda, occasioned by an atom of water becoming basic to the acid, which before was constitutional to the salt (page 353).

The bipyrophosphate of soda undergoes several changes, under the influence of heat before it becomes metaphosphate. At a temperature of 500° , the salt becomes nearly anhydrous, and affords a solution which is *neutral* to test paper, but in other respects resembles the bipyrophosphate. But at tempe-

ratures which are higher, although short of a red heat, the salt being anhydrous, appears to have lost its solubility in water; at least it is not affected at first when thrown in powder into boiling water, but gradually dissolves by continued digestion, and passes into the preceding variety.—(Phil Trans. 1833, p. 275.)

Borax, Biborate of soda; $\text{Na O}, 2\text{BO}_3 + 10\text{HO}$; 1263.3. + 1125 or 101.23 + 90.—This salt is met with in commerce in large hard crystals. It is found in the water of certain lakes in Transylvania, Tartary, China, and Thibet, and is deposited in their beds by spontaneous evaporation. It is imported from India in a crude state, and enveloped in a fatty matter, under the name of *Tinkal*, and afterwards purified. But nearly the whole borax consumed in England is at present formed by neutralising with carbonate of soda, the acid from the boracic lagoons of Tuscany. The ordinary crystals of borax are prisms of the oblique system, containing 10 atoms of water, which are not efflorescent when free from carbonate (Mr. O. Sims); but it also crystallizes at 133° in regular octohedrons, which contain only 5 atoms of water. This salt has a sweetish, alkaline taste; for although containing an excess of acid, it has an alkaline reaction, like the bicarbonate of soda.

The anhydrous salt is very fusible by heat, and forms a glass. This glass possesses the property of dissolving most metallic oxides, the smallest portions of which colour it. As the metal may often be discovered by the colour, borax is valuable as a flux in blow-pipe experiments. As pieces of metal could not be soldered together, if covered by oxide, borax is fused with the solder upon the surface of the metals to be joined, to remove the oxide. Borax is also a constituent of the soft glass, known as jewellers' paste, which is coloured to imitate precious stones. But the most considerable consumption of this salt is at the potteries, in the formation of a glaze for porcelain.

A neutral borate of soda was formed by Berzelius by calcining strongly 1 eq. of borax with 1 eq. of carbonate of soda, when carbonic acid is expelled. The solution yields a salt belonging to the oblique prismatic system, of which the formula is, $\text{NaO}, \text{BO}_3 + 8\text{HO}$. When heated, it fuses in its water of crystallization, and is expanded into a vesicular mass of extraordinary magnitude, by the vaporisation of that water.

When borax is fused with carbonate of soda in excess, the

quantity of carbonic acid which escapes indicates the formation of a borate, $3\text{NaO} + 2\text{BO}_3$, but which has not been farther examined.

A salt is said to exist, formed of $\text{NaO} + 4\text{BO}_3$, but to crystallize with difficulty, formed on combining borax with a quantity of boracic acid equal to what it already contains. M. Laurent has also shewn that a sexborate of soda exists in solution, but is not crystallizable*. The borates of potash have also been examined by Laurent. The sexborate crystallizes well; its formula is $\text{KO}, 6\text{BO}_3 + 10\text{HO}$. A triborate is represented by $\text{KO}, 3\text{BO}_3 + 8\text{HO}$; the biborate corresponds in composition with octohedral borax, but has, notwithstanding, a different and incompatible form.

Silicates of soda.—When the earth silica (page 314) is thrown into carbonate of potash or soda, in a state of fusion by heat, a fusible silicate is formed, in which, judging from the quantity of carbonic acid expelled, 3 eq. of alkali are combined with 2 of silica, or the oxygen in the alkali is to that in the silica as 1 to 2. This silicate dissolves in the clear and liquid carbonate. When on the other hand a greater proportion of silica is fused with the carbonate, the whole carbonic acid of the latter is expelled, and the excess of silica then dissolves in the silicate. The silica and silicate of such mixtures do not separate by crystallization, but uniformly solidify together, on cooling, as a homogeneous glass, whatever their proportions may be. It is thus impossible to obtain alkaline silicates, which are certainly definite combinations. A mixture of silica with potash or soda, in which the oxygen of the former is to that of the latter as 18 to 1, is said still to be fusible by the heat of a forge; but when the proportion is as 30 to 1, the mixture merely agglutinates or frits. These combinations, even with a large quantity of silica, continue to be soluble in water.

A compound, known as *soluble glass*, is obtained by fusing together 8 parts of carbonate of soda (or 10 of carbonate of potash) with 15 of fine sand and 1 of charcoal. The object of the charcoal is to facilitate the combination of the silica with the alkali, by destroying the carbonic acid, which it converts into carbonic oxide. This glass, when reduced to powder is not attacked by cold water, but is dissolved by 4 or 5 parts of

* An de Ch. et de Ph. t. 67, p. 218.

boiling water. The solution may be applied to objects of wood, and when dried by a gentle heat forms a varnish, which imbibes a little moisture from the air, but is not decomposed by carbonic acid, nor otherwise alterable by exposure. Stuffs impregnated with the solution lose much of their combustibility, and wood is also defended by it, to a certain degree, from combustion.

GLASS.

The alkaline silicates, cooled quickly or slowly, never exhibit a crystalline structure, but are uniformly vitreous. They are the bases of the ordinary varieties of glass, which contain earthy silicates besides, but appear to owe the vitreous character to the silicates of potash and soda. The silicate of lime and the silicate of the protoxide of iron crystallize on cooling, so does the silicate of lead, unless it contains a large excess of oxide of lead. The addition of the silicate of potash or soda deprives them entirely of this property; the silicate of alumina considerably diminishes it. But if silicates of potash or soda are heated for a long time, the alkali may in part escape in vapour, and if other bases exist in the compound, it then often assumes a crystalline structure on cooling. The alkaline silicates by themselves are soluble in water, and decomposed by acids; the silicate of lime is also dissolved by acids, but the double silicates, on the contrary, resist the action of acids, particularly when they contain an excess of silica. The following table exhibits the composition of the best known kinds of glass, from the analyses of Dumas and of Faraday :—

COMPOSITION OF VARIETIES OF GLASS.

	Silica.	Potash.	Lime.	Ox. lead.	Alumina.	Water.
Bohemian glass	69	12	9	0	10	0
Crown glass .	63	22	12	0	3	0
Window glass .	69	11 soda	13	0	7	0
Bottle glass .	54	5	29	6 ox. iron.	0	0
Flint glass . .	45	12	0	43	0	0
Crystal . . .	61	6	0	33	0	0
Strass . . .	38	8	0	53	1	0
Soluble glass .	62	26	0	0	0	12

Silicate of soda and lime.—To form window-glass 100 parts of a quartz sand are taken, with 35 to 40 parts of chalk, 30 to

35 parts of carbonate of soda and 180 parts of broken glass. These materials are first fritted, or heated so as to cause the expulsion of water and carbonic acid, and to produce an agglutination of their particles, and afterwards completely fused in a large clay crucible of a peculiar construction. For the first formation of the glass a higher temperature is required, than that at which it is most thick and viscid, and in the proper condition for working it. At the latter temperature, the substance possesses an extraordinary degree of ductility, and may be drawn out into threads so fine as to be scarcely visible to the eye. A portion of the plastic mass, on the extremity of a blow-pipe, may be expanded into a globular flask, and prest or bent into vessels of any form, which may be pared and fashioned by the scissors. At a lower temperature, glass vessels become rigid, and when cold brittle in the extreme, unless they be *annealed*, that is, kept for several hours at a temperature progressively lowered from the highest degree which the glass can bear without softening, to the temperature of the atmosphere. The well-known glass tears, or Prince Rupert's drops, as they are also called, which are made by allowing drops of melted glass to fall into water, illustrate the peculiar properties of unannealed glass. The surface becoming solid by the sudden cooling, while the interior is still at a high temperature and consequently dilated, the drop is of greater volume than it would be if cooled slowly and equally throughout its mass. Its particles are thus in a state of extreme tension, and an injury to any part causes the whole mass to fly to pieces. The fracture of unannealed vessels, which is the immediate consequence of scratching their surface, has been compared to the effect upon a sheet of cloth forcibly stretched, of injuring its edge in the smallest degree by a knife or scissors. It then ceases to preserve its integrity by resisting the tension, and is torn across. The relative proportions of the ingredients of this and other species of glass is subject to some variation. But the oxygen in the bases of window-glass is to the oxygen of the silica, nearly as 1 to 4. This glass has a green tint, which is very obvious in a considerable mass of it, occasioned in part, it may be, by the impurities of the materials, but a certain degree of which appears to be essential to a soda-glass. For in all the colourless and finer varieties of glass, it is necessary to use potash.

Silicates of potash and lime.—Plate-glass used for mirrors,

crown-glass, and the beautiful Bohemian glass are of this composition. In the most remarkable varieties the oxygen of the bases is to that of the acid as 1 to 4, and the oxygen of the lime to that of the potash in proportions which vary from 1 and $\frac{2}{3}$, to 1 and 1. This is the glass of most difficult fusibility, and therefore most suitable for the combustion tubes employed in organic analysis. From its purity, and the absence of oxide of lead, it is also made the basis of most coloured glasses, and of stained glass. To produce coloured glasses certain metallic oxides are mixed with the fused glass in the pot, oxide of cobalt for instance, for a blue colour, oxide of copper for green, peroxide of manganese for purple, and peroxide of uranium for a delicate lemon yellow tint. Arsenious acid and peroxide of tin render glass white and opaque, like enamel. In stained glass, on the other hand, the metallic oxides are merely applied with proper fluxes to the surface of the glass, which is then exposed in an oven to a temperature sufficient to fuse the colouring matter. Different shades of yellow and orange are thus produced by means of oxide of silver, and a superb ruby red by a proper, but difficult, application of suboxide of copper.

Silicates of potash and lead.—These substances enter into the composition of the purer and more brilliant species of glass in use in this country, such as that called crystal, of which most drinking vessels are made, flint-glass for optical purposes, and strass, which is employed in imitations of the precious stones. For crystal, the materials are taken in the following proportions, 120 parts of fine sand, about 40 of purified potashes, 35 of litharge or minium, and 12 of nitre. In this glass, the oxygen of the bases is to that of the silica, as 1 to a number which may vary from 7 to 9, and the oxygen of the potash is to that of the oxide of lead, as 1 to a number varying from 1 to 2.5. In flint-glass and in strass, the oxygen of the bases is to that of the silica as 1 to 4, and the oxygen of the potash is to that of the oxide of lead as 2 to 3 in flint-glass, and as 1 to 3 in strass, (Dumas). The more oxide of lead glass contains, the higher its density; the density of this kind of glass exceeding 3.6, while that of the Bohemian glass does not rise higher than 2.4. Glass containing oxide of lead is recommended by its greater fusibility and softness, by which it is more easily fashioned into various forms, and by its great brilliancy, which is remarkable in lustres and other objects of cut glass. The presence of lead

in glass is at once discovered by its surface acquiring a metallic lustre when heated to redness in the reducing flame.

Silicates of alumina, of the oxides of iron, magnesia, and potash or soda.—Green or bottle glass, of which wine-bottles, carboys, and glass articles of low price consist, is a mixture of these silicates. It is formed of the cheapest materials, such as sand, with soap-makers' waste, lime that has been used to render alkali caustic, &c. In the bottle-glass of this country the small quantity of alkali is chiefly soda. The alkaline sulphates when fused with silica and carbonaceous matter, lose their sulphuric acid, and become silicates; even common salt is decomposed by the united action of silica and the aqueous vapour in flame, but much of it is lost from its own volatility. The proportion of silica to the bases is much less in this than in the other kinds of glass, the oxygen of the former being to the latter as 2 to 1; and the oxygen of the alumina and peroxide of iron equal to that of the potash and lime. This glass is in fact a mixture of neutral and subsilicates, and is more apt than any of the preceding species to assume a crystalline structure when maintained long in a soft condition by heat. A bottle of green glass may be devitrified, or converted into what is called Reaumur's porcelain, by enveloping it in sand, and placing it where its temperature is kept high for several weeks, as in a brick kiln or porcelain furnace. It has been supposed that the glass loses its alkali in these circumstances, and is thus more easily crystallized, but the proportion of alkali is found undiminished after the change. Glass of all kinds, however, when strongly and repeatedly heated loses alkali, from its volatility; the glass then becomes harder and less fusible, and is not so easily wrought, a circumstance which may sometimes be remarked in blowing a bulb upon a tube which has been too long exposed to the blow-pipe flame.

SECTION III.

LITHIUM.

Eq. 80.33 or 6.44; L.

Lithium is the metallic basis of a rare alkaline oxide lithia discovered in 1818 by Arfwedson*. The name lithia (from

* An. de Ch. et de Ph. t. 10.

λίθιος, stony,) was applied to it, from its having been first derived from an earthy mineral. The metal was obtained by Davy by the voltaic decomposition of lithia, and observed to be white, resembling sodium, and to be highly oxidable. The equivalent of lithium is much smaller than that of any other metal, and its oxide has therefore a high saturating power.

Lithia; LO.—The only known oxide of lithium is a protoxide. It exists in small quantities in the minerals spodumene, or triphane, petalite, and lepidolite, of which the latter can be procured in largest quantity. The separation of lithia from this mineral rests upon its decomposition by means of lime at a high temperature, and the formation of silicate of lime. By a protracted digestion of the ignited mass in boiling lime-water, the liberation of the lithia is completed, and it dissolves in that liquid. The oxides in solution are converted into chlorides, by the addition of hydrochloric acid, and must be submitted to several additional operations to separate iron, lime, and potash. The chloride of lithium is finally taken up by absolute alcohol, in which the chloride of potassium is not soluble. For the necessary directions for conducting this difficult process, I must refer to Berzelius.—(*Traité*, t. 1 p. 303.)

The hydrate of lithia resembles hydrate of potash in causticity, but is less soluble in water, and loses its combined water at an elevated temperature. Sulphur acts upon it in the same manner as upon potash.

The chloride is very soluble in water, as well as in absolute alcohol, and fuses at a high temperature.

The carbonate of lithia has a certain degree of solubility, and its solution has an alkaline reaction, properties upon which the claim of lithia to be ranked among the alkalies, instead of the alkaline earths, is chiefly rested. The fluoride of lithium has the sparing solubility of the carbonate.

The sulphate of lithia is soluble, and presents itself in fine crystals, which are persistent in air. The nitrate and acetate are both very soluble and deliquescent.

The neutral phosphate of lithia is slightly soluble in water, but considerably more so than the double phosphate of lithia and soda, which remains as an insoluble powder when the solution of lithia is evaporated to dryness with that of phosphate of soda. Hence phosphate of soda is used as a test of lithia. The salts of lithia are also recognised, when heated on platinum wire before the blow-pipe, by tinging the flame of a red colour.

ORDER II.

METALLIC BASES OF THE ALKALINE EARTHS.

SECTION IV.

BARIUM.

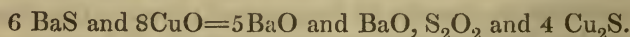
Eq. 856.9 or 68.66; Ba.

Barium, the metallic basis of barytes, was obtained by Davy in 1808, by the voltaic decomposition of moistened carbonate of barytes in contact with mercury; it may likewise be procured by passing potassium in vapour over barytes heated to redness in an iron tube, and afterwards withdrawing the reduced barium, which the residue contains, by means of mercury. The latter metal is separated by distillation in a retort, care being taken not to raise the temperature to redness, for then the barium decomposes glass. Barium is a white metal like silver, fusible under a red heat, denser than oil of vitriol in which it sinks. It oxidates with vivacity in water, disengages hydrogen, and is converted into barytes. It is named barium (from *βαρύς*, heavy), in allusion to the great density of its compounds.

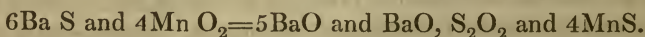
Barytes: BaO; 956.9 or 76.66.—This earth exists in several minerals, of which the most abundant are sulphate of barytes or heavy spar, and the carbonate of barytes or witherite. The earth is obtained in the anhydrous condition and pure, by calcining nitrate of barytes, at a bright red heat, in a porcelain retort, or in a well covered crucible of porcelain or silver, but not of platinum. If the calcination is not carried sufficiently far, a combination remains of barytes and nitrous oxide (Berzelius), which has been mistaken for peroxide of barium. The iodate of barytes also may be calcined in a porcelain retort, for barytes; it is, I find, more easily decomposed than the nitrate, and has not the troublesome property of fusing and swelling up, when heated, which the latter salt possesses. The iodine comes off, with oxygen, and may be recovered. Iodate of barytes itself is obtained, as an insoluble precipitate, on adding chloride of barium to iodate of soda (page 390). Barytes is a grey powder, of which the density is about 4. When heated to redness in a porcelain tube, and oxygen passed over it, it ab-

sorbs that gas with avidity, and becomes peroxide of barium, the compound for the preparation of which anhydrous barytes is chiefly required. This earth slakes and falls to powder, when water is thrown upon it, combining with one equivalent of water with the evolution of much heat.

Hydrate of barytes is a valuable reagent. Of the different processes for this substance, one of the most convenient is that from the native sulphate. This is a soft mineral and easily reduced to an impalpable powder, which is intimately mixed with 1-3rd of its weight of coal-dust, or coal pounded and sifted; the mixture is introduced into a cornish crucible, and exposed in a furnace to a bright red heat for an hour. The sulphate is converted by this treatment into sulphuret of barium; the last salt is dissolved out of the black residuary mass, by boiling water, and the solution, which generally has a yellowish tint but is sometimes colourless, is filtered while still hot. The solution, if strong, may crystallize on cooling, in thin plates. As it also absorbs oxygen from the air, and returns to the state of sulphate of barytes, it must not be exposed long in open vessels. To a boiling solution of sulphuret of barium in a flask, black oxide of copper from the nitrate is added, in successive small portions, till a drop of the liquid ceases to blacken a solution of lead, and precipitates it entirely white; the liquid then contains only hydrate of barytes in solution. It may immediately be filtered, with little access of air, as it absorbs carbonic acid. The decomposition in this process, for which we are indebted to Dr. Mohr of Coblenz, is rather complicated. Six eq. of sulphuret of barium and 8 of oxide of copper producing 5 of barytes, 1 of hyposulphite of barytes, and 4 of subsulphuret of copper:



Peroxide of manganese may be substituted in this process for oxide of copper, but generally gives a solution of barytes coloured by some impurity. The reaction is then similar*:



If the solution of sulphuret of barium has been concentrated, the greater part of the hydrate of barytes separates on cooling, in voluminous and transparent crystals. It is soluble in 3

* Liebig's Annalen, v. 27, p. 21.

parts of boiling water, and in 20 parts of water at 60°. Mr. Smith finds this hydrate to contain 9HO, of which it loses 7, by a moderate heat, and 1 additional, by a stronger heat. Barytes retains 1 eq. of water with great force like the fixed alkalies. This combination is fusible a little below redness, and runs like an oil; it congeals into a crystalline mass, which attracts carbonic acid very slowly from air, and is therefore the most favourable condition in which to preserve hydrate of barytes.

The solution of barytes is strongly caustic, although less so than potash or soda; and, in common with all the soluble preparations of barium, it is poisonous. It is used to remove carbonic acid from air and other gases (page 280). Barytes, whether free or in combination with an acid, as a soluble salt, is discovered by means of sulphuric acid, which throws down sulphate of barytes, a compound not decomposed by, nor soluble in, nitric and hydrochloric acids.

Peroxide of barium; Ba O_2 ; 1056.9 or 84.69.—This compound is prepared by exposing anhydrous barytes to pure oxygen at a red heat; or by heating pure barytes to low redness in a porcelain crucible, and then gradually adding chlorate of potash, in the ratio of about 1 part of the latter to 4 of the former. The chloride of potassium is removed, by cold water, from the peroxide of barium formed at the same time, while the latter forms a hydrate with 6HO (Liebig and Wöhler.) Peroxide of barium, when decomposed by dilute acids with proper precautions, affords peroxide of hydrogen.

Chloride of barium; $\text{Ba Cl} + 2\text{HO}$; 1299.6 + 225, or 104.83 + 18.—A re-agent of constant use, which is obtained by dissolving native carbonate of barytes in pure hydrochloric acid diluted with 3 or 4 times its bulk of water, or by neutralising sulphuret of barium by the same acid. It crystallizes from a concentrated solution in flat four-sided tables, bevelled at the edges, very like crystals of heavy spar. The crystals contain 2 eq. of water, (14.75 per cent), which they lose below 212°. They are said to be soluble in 100 parts of anhydrous alcohol: 100 parts of water dissolve 43.5 at 60°, and 78 at 222°, which is the boiling point of the solution.

Carbonate of barytes; $\text{Ba O}, \text{CO}_2$; 1233.3, or 98.83.—This salt consists in 100 parts of 22.41 carbonic acid, and 77.59 barytes. The density of the native carbonate is 4.331. It retains its carbonic acid at the highest temperatures. The

precipitated carbonate loses its carbonic when calcined at a white heat, in contact with carbonaceous matter. It is obtained in greater purity when precipitated by the carbonate of ammonia, than by the carbonate of potash or soda, portions of which are apt to go down in combination with carbonate of barytes. Although reputed an insoluble salt, carbonate of barytes is soluble in 2300 parts of boiling water, and in 4300 parts of cold water. It is still more soluble in water containing carbonic acid, and is highly poisonous. The precipitated carbonate of barytes is employed in the analysis of siliceous minerals, containing an alkali, which are not soluble in an acid. The mineral, in the state of an impalpable powder, is intimately mixed with 4 or 5 times its weight of this carbonate, and exposed in a platinum crucible to a white heat, which occasions a semi-fusion of the mixture and the decomposition of the silicates; the mineral afterwards dissolving entirely in an acid, with the exception of its silica.

Sulphate of barytes; Ba O, SO_3 ; 1458, or 119.56.—This salt consists, in 100 parts, of 34.37 sulphuric acid and 65.63 barytes. The density of heavy spar, or the native sulphate, varies from 4 to 4.47. It occurs in considerable quantities, in trap and other igneous rocks, forming often veins of several feet in thickness, and miles in extent. It is mined for the purpose of being substituted for carbonate of lead, or being mixed with that substance, when used as a pigment. When chloride of barium is added to sulphuric acid, or to a soluble sulphate, at the boiling temperature, sulphate of barytes precipitates readily, in a dense crystalline powder, which may easily be washed and collected on a filter. It is completely insoluble in water and dilute acids; but is soluble in concentrated and boiling sulphuric acid, from which it crystallizes on cooling. Precipitated sulphate of barytes is partially decomposed in a concentrated and boiling solution of carbonate of potash or soda, and carbonate of barytes formed.

Nitrate of barytes; Ba O, NO_5 ; 1633.9, or 130.93.—This salt crystallizes in fine transparent octohedrons, which are anhydrous. It is obtained by dissolving carbonate of barytes in nitric acid, diluted with 8 or 10 times its weight of water, or by mixing the acid, also in a diluted state, with the solution of sulphuret of barium. It requires 12 parts of water at 60° , and 3 or 4 of boiling water for solution; it is insoluble in alcohol.

The nitrate of barytes is employed as a re-agent, and also in procuring pure barytes.

The chlorate and hyposulphate of barytes are soluble, the iodate, sulphite, hyposulphite and phosphates of barytes, insoluble salts.

SECTION V.

STRONTIUM.

Eq. 547.3, or 43.85; Sr.

Strontium is prepared in the same way as barium, which it greatly resembles. It is a white metal, denser than oil of vitriol. It derives its name from Strontian, a mining village in Argyleshire.

Strontian, Strontia, or Strontites; Sr O; 647.3, or 51.85.—The native carbonate of strontian was first distinguished from carbonate of barytes by Dr. Crawford, in 1790, who conceived the idea that the former mineral might contain a new earth. This conjecture was verified in 1793, by Dr. Hope;* and much about the same time also by Klaproth. The earth, strontian, is to barytes what soda is to potash. It occurs in nature as carbonate and sulphate, but not abundantly. Strontian may be prepared by a strong calcination of the native carbonate in contact with carbon. It is lighter than barytes, and has a taste which is less acrid and caustic, but stronger than that of lime. It is said not to be poisonous. The hydrate crystallizes with 9HO, but retains only one equivalent at 212° (Mr. Smith.) This last hydrate enters into fusion at a very high temperature, without losing its combined water. The pure earth, like barytes, is infusible. The crystallized hydrate requires 52 parts of water to dissolve it at 60°, but only twice its weight at 212°.

The soluble salts of strontian are prepared from the carbonate. They are precipitated by sulphuric acid and by soluble sulphates, but not so completely as the salts of barytes, the sulphate of strontian having a small degree of solubility. Hence, when sulphate of soda is added in excess to a salt of strontian, and the precipitate separated by filtration, so much sulphate of

* Edinburgh Transactions, iv, 14.

strontian remains in solution, that the liquid yields a white precipitate with carbonate of soda (Dr. Turner.) Most of the salts of strontian, when heated on platinum wire before the blow-pipe, communicate a red colour to the flame. Barytes and strontian in solution, may be separated by hydrofluosilicic acid, which precipitates barytes, but forms with strontian a salt very soluble in a slight excess of acid. Hyposulphite of strontian being soluble, while hyposulphite of barytes is insoluble, these earths may also be separated by means of hyposulphite of soda.

Peroxide of strontium, obtained by Thenard in brilliant crystalline scales, on adding peroxide of hydrogen to a solution of strontian. It contains two eq. of oxygen.

Chloride of strontium crystallizes in slender prisms, which contain $9\text{H}_2\text{O}$, and are slightly deliquescent. This salt is soluble in three-fourths of its weight of cold water, and in all proportions in boiling water. At the ordinary temperature, it dissolves in 24 parts of anhydrous alcohol, and in 19 parts of boiling alcohol. In this respect, it differs from chloride of barium, which is insoluble in alcohol. Chloride of strontium communicates to flame a fine red tint. In the anhydrous condition, this chloride absorbs 4 eq. of ammonia, and becomes a white bulky powder.

Carbonate of strontian forms the mineral *strontianite*, which generally has a fibrous texture, and is sometimes transparent and colourless, but generally has a tinge of yellow or green. Its density varies from 3.4 to 3.726. This salt is said to be soluble in 1536 parts of boiling water. It is more soluble in water containing carbonic acid, and occurs in some mineral waters. It retains its carbonic acid when calcined.

Sulphate of strontian is known as *celestine*, and occurs in regular crystals of the same form as sulphate of barytes. Its density is about 3.89. It is not sensibly soluble in cold water, but is said to be soluble in 3840 times its weight of boiling water. This mineral is found in considerable quantity associated with volcanic sulphur, and in other formations. The various compounds of strontium may be prepared from it, precisely in the same manner as those of barium from the sulphate of barytes.

Hyposulphite of strontian is crystallizable, and soluble in 4 parts of cold, and $1\frac{3}{4}$ parts of boiling water. It loses 31 per

cent of water of crystallization between 122° and 140° , without any other change.

Nitrate of strontian generally crystallizes in octohedrons, which are anhydrous, but it may be obtained at a low temperature in crystals of another form, which contain 5HO . The anhydrous salt dissolves in 5 parts of cold water, and in $\frac{1}{2}$ part of boiling water. A deflagrating mixture, which produces an intensely red illumination, is formed of 40 parts of nitrate of strontian, 13 parts of flowers of sulphur, 5 parts of chlorate of potash, and 4 parts of sulphuret of antimony.

The salts of barytes, strontian and lead are strictly isomorphous, and greatly resemble each other in solubility and other properties.

SECTION VI.

CALCIUM.

Eq. 256, or 20.52; Ca.

Davy obtained evidence of the existence of this metal, and of its analogy to the preceding metals. It is the basis of lime. The name applied to it is derived from calx.

Lime; Ca O ; 356, or 28.52.—Uncombined lime, or quicklime, as it is termed in the arts, is obtained by heating masses of limestone (carbonate of lime) to redness in a lime-kiln, or open fire. The escape of the carbonic acid is favoured by the presence of the aqueous vapour and gases of the fire, into which that gas can diffuse (page 187). In a covered crucible, carbonate of lime may be fused by heat without decomposition. The lime remains in porous masses, which may easily be separated from the ashes of the fuel, and are sufficiently hard to be transported from place to place without falling to pieces. Although these masses appear light, the density of lime is not less than 2.3, or even 3.08, according to Roget and Dumas. Water thrown upon them, is first imbibed, and afterwards combines with the lime, which falls to powder in the state of hydrate, and is then said to be slaked. In this combination, the temperature rises sufficiently high to char and kindle wood; but the hydrate is decomposed, and lime is made anhydrous by a red heat. From its affinity for water, quicklime is applied to deprive certain liquids, such as alcohol,

of the water they contain. It is obtained in a suitable state of division for that purpose, by submitting to calcination in a crucible the hydrate of lime itself, or by calcining 2 parts of hydrate mixed with 3 of pulverulent chalk. For pure lime, the crystallized carbonate should be calcined, such as calcareous spar, or Carrara marble. Lime, in common with other infusible earths, phosphoresces strongly when heated to full redness.

The hydrate of lime contains 1 eq. of water, which it loses at a low red heat. It is sparingly soluble in water, but more soluble in cold than in hot water. According to Dalton, lime-water formed at 60° , 130° and 212° , contains 1 grain of lime in 778, 972 and 1270 grains of water. Hence, water saturated in the cold, deposits hydrate of lime, when boiled. By evaporating the solution in vacuo, Gay-Lussac obtained hydrate of lime in small transparent crystals of the hexahedral form. The *milk* or *cream* of lime is merely the hydrate diffused through water. Lime-water has a harsh acrid taste, is alkaline, and, to a certain extent, caustic. It precipitates carbonic, silicic, boracic and phosphoric acids from solutions of their alkaline salts. It dissolves oxide of lead. Lime-water absorbs carbonic acid rapidly from the air, and becomes covered by a pellicle of carbonate of lime. Hydrate of lime has the same property, absorbing about half an equivalent of carbonic acid with avidity, but not acquiring quite so much as three-fourths of an equivalent by 2 or 3 weeks' exposure to an atmosphere of the gas. Fuchs observes, that when hydrate of lime is exposed to air, it absorbs only half an equivalent of carbonic acid, and a definite compound of hydrate and carbonate is formed. In the anhydrous condition, lime exhibits no affinity for carbonic acid.

Lime is characterized by affording a bulky precipitate of sulphate of lime, when sulphuric acid is added to its soluble salts. But as the sulphate of lime has a certain degree of solubility, this precipitate does not appear in very dilute solutions of these salts, nor in lime-water, a property by which lime may be distinguished from barytes and strontian. Sulphate of lime may also, when separated, be re-dissolved by the addition of nitric acid. Lime is entirely precipitated from neutral solutions, by oxalate of ammonia, the oxalate of lime being completely insoluble. In the quantitative estimation of this earth, it is

therefore generally thrown down as oxalate, and afterwards obtained as carbonate of lime, by heating the oxalate nearly to redness in a platinum crucible, in which a small fragment of carbonate of ammonia is dissipated at the same time, to prevent any lime becoming caustic by loss of carbonic acid.

Lime is applied to a variety of useful purposes in ordinary life and in the arts, of which the most important are its applications as mortar and as a manure for land. In the last, lime does not act as an aliment of plants, but is useful in accelerating the decomposition of the insoluble organic matter which soil contains, and thereby rendering it capable of sustaining vegetable life. Hence, the extraordinary fertility which lime develops in soils containing peaty matter. In the formation of mortar, the hydrate of lime is mixed with 2 parts of coarse, or 3 parts of fine sand, and made into a paste with water. In building, a stone is laid upon a bed of this paste, which it compresses by its weight, imbibing moisture also from the mortar, which escapes principally through the porous stone. On drying, the mortar binds the stones between which it is interposed, and its own particles cohere so as to form a hard mass, solely by the attraction of aggregation, for no chemical combination takes place between the lime and sand, and the stones are simply united as two pieces of wood are by glue. The sand is useful in rendering insignificant by its mass the contraction of the mortar on drying, and also, from the large size of its grains, in rendering the dry mortar less short and friable. The mortar is subject to an ulterior change, from the slow absorption of carbonic acid, but even in the oldest mortar, the conversion of the hydrate of lime into carbonate is never complete.

Some limestones, containing about 20 per cent of clay or silicate of alumina, afford lime which possesses a valuable property, that of forming with water a mass which becomes solid in a few minutes, and therefore hardens in structures covered by water. An excellent hydraulic mortar of this kind is obtained from concretionary masses found in marle, and also as isolated blocks in the bed of the Thames. This lime being burnt, ground and sifted, when mixed with water to form a paste, sets as quickly as Paris plaster; its solidity increases with the time it has been submerged, and it ends by acquiring the hardness of limestone. Sand is added to it when it is used

as common mortar, or in covering buildings to imitate stone. From the minute division of the silica and alumina in this mortar, their combination with lime is more likely to occur than in ordinary mortar. Still the first setting of hydraulic mortar seems to be due simply to the fixation of water, and formation of a solid hydrate like gypsum. Hydraulic mortar is sometimes made by mixing together clay and chalk, and calcining the mixture, or more frequently by adding to hydrate of lime puzzolano ground to fine powder. The latter is a substance of volcanic origin, composed principally of pumice, of which a stratum is excavated in the neighbourhood of Pozzuoli near Naples. The mortar which it makes with lime has obtained the name of Roman cement.

The hydrate of *peroxide of calcium* precipitates on adding lime-water, drop by drop, to a solution of peroxide of hydrogen. It contains, according to Thenard, 2 eq. of oxygen.

The *protosulphuret of calcium* is procured by decomposing sulphate of lime at a red heat, by hydrogen or charcoal. When newly prepared, it phosphoresces in the dark. It is sparingly soluble in water. When hydrate of lime is boiled with sulphur and water, and the liquor allowed to cool before it is completely saturated with sulphur, yellow crystals separate from it, which are a *bisulphuret of calcium*, combined with 3HO, according to the observations of Herschel. When lime, or protosulphuret of calcium is boiled with excess of sulphur, it dissolves sulphur till a *pentasulphuret of calcium* is formed, which resembles in properties the corresponding degree of sulphuration of potassium.

Phosphuret of calcium.—Small fragments of quicklime being heated to redness, by a spirit lamp, in a small matrass with a long neck, and fragments of phosphorus dropt into the same vessel, a mixture is obtained of phosphate of lime and phosphuret of calcium. The compound has a chocolate brown colour. When the temperature is raised too high, the affinities change, and phosphorus escaping in vapour, nothing but lime remains. This substance decomposes water, when thrown into it, with effervescence, from the escape of phosphuretted hydrogen, which takes fire spontaneously, while hypophosphite of lime is dissolved by the water.

Chloride of calcium; Ca Cl ; 698.7, or 55.98.—Obtained by neutralising hydrochloric acid with carbonate of lime, or as a

residue in several processes; a concentrated solution affords crystals in large striated four-sided prisms, which contain 6 eq. of water. Dried with stirring, at 300° , it affords a crystalline powder, containing 2 eq. water, which produces an intense degree of cold when mixed with snow (page 44.) The crystals are very soluble and exceedingly deliquescent. The salt is made anhydrous by heat, and undergoes the igneous fusion at a red heat. The liquid chloride is poured upon a slab, and the transparent cake of solid salt immediately broken into pieces, and preserved in a stoppered bottle. It is much employed, from its great affinity for water, to dry gases and absorb moisture. Chloride of calcium always acquires by fusion a slight but sensible alkaline reaction, from partial decomposition; on which account Liebig prefers the salt strongly dried, but not fused, as the hygrometric agent in organic analysis. Ten parts of anhydrous alcohol dissolve 7 of chloride of calcium, at the boiling point, and the solution, in cold weather, affords crystals in rectangular scales, which are an alcoate, containing about 60 per cent of alcohol, instead of water of crystallization. Anhydrous chloride of calcium likewise absorbs 4 equivalents of ammoniacal gas.

A solution of chloride of calcium when boiled with *hydrate of lime* dissolves that substance, and the solution filtered hot, deposits long flat and thin crystals, which contain 49 per cent of water. The empirical formula of this salt is $\text{Ca Cl} + 3\text{Ca O} + 15\text{H O}$. The salt is decomposed by water and alcohol.

A compound of chloride of calcium with *oxalate of lime*, containing water of crystallization is obtained in good crystals, which are persistent in air, by dissolving oxalate of lime to saturation in hot hydrochloric acid and allowing the solution to cool. It consists of 1 eq. of each salt, with 7 eq. of water. Oxalate of lime is known to combine with 2 eq. of water, of which 1 eq. appears to remain in this double salt, while the other is replaced by chloride of calcium carrying its 6 atoms of water of crystallization along with it. A similar replacement is observed in the formation of quadroxalate of potash (page 172). This salt becomes anhydrous without decomposition at 266° (130° cent). It is decomposed by pure water.

Fluoride of calcium, fluor spar; Ca F ; 489.8 or 39.25.—This salt occurs in nature, massive and in transparent crystals, which are cubes or octohedrons. It is often of beautiful colours, generally green or purple, and is cut into ornaments. When

heated gently on a plate of metal, it becomes very luminous in the dark, or phosphoresces. Fluoride of calcium is insoluble in water, and is obtained in a granular condition, when hydrofluoric acid is neutralised by freshly precipitated carbonate of lime. But when a neutral salt of lime is mixed with a soluble fluoride, the fluoride of calcium appears as a translucent gelatinous mass. This fluoride, whether artificial or natural, is not decomposed by sulphuric acid at a low temperature, but imbibes that acid, and forms a thick ropy liquid. At 104° (40° cent.) this mixture begins to decompose and emits hydrofluoric acid.

SALTS OF LIME.

Carbonate of lime; Ca CO_2 ; 632.5 or 50.68.—This is one of the most abundantly diffused salts in nature, forming the basis of limestones, marbles, marles, coral-reefs, shells, &c. It is always anhydrous, and occurs in two incompatible crystalline forms, the rhomboidal crystal of calc-spar, which with its numerous modifications is much the most abundant, and the six-sided prism of arragonite, isomorphous with carbonate of strontian, which may be readily recognized by falling to powder when heated. The grains of this powder have the form of calc-spar. The density of carbonate of lime in these two forms is sensibly different, that of calc-spar being 2.719, and of arragonite 2.949 (G. Rose). Carbonate of lime consists in 100 parts, of 56.29 lime and 43.71 carbonic acid.

Carbonate of lime may also be obtained in the state of a hydrate, by heating together 1 part of hydrate of lime, 3 of sugar, and 6 of water, filtering the solution and leaving it to cool in a shallow vessel. In twenty-four hours crystals appear upon the surface of the liquid, and in fifteen days the whole lime is generally converted into hydrated carbonate, in the form of sharp transparent rhombs. The carbonic acid is absorbed from the atmosphere. These crystals contain 5 eq. of water. By boiling them in anhydrous alcohol, a second definite hydrate is obtained containing 3 eq. of water, as ascertained by Pelouze. These correspond in composition with two crystalline hydrates of carbonate of magnesia.

Carbonate of lime is considered an insoluble salt, although according to Bucholz it dissolves in 16 or 24 thousand times its weight of pure water. But it is soluble in water containing carbonic acid, and is generally present in the water of wells, and

in some mineral waters to a considerable extent. It is deposited from the latter, when exposed to air, in a gradual manner and in possession of a crystalline structure, forming stalactites in mountain caverns, and calcareous petrifications, when it flows over wood and other organic and destructible matters, of which it preserves the form. It is decomposed with effervescence by acids. At a red heat it parts with carbonic acid and is converted into quicklime in the manner already described.

A crystalline mineral was discovered by Boussingault at Merida in America, which he ascertained to be a double carbonate of soda and lime, with 5 eq. of water, and named *gay-lussite*, in honour of Gay Lussac. It may be made anhydrous by heat, and its two salts are then separated by water.

Sulphate of lime, gypsum; $\text{CaO}, \text{SO}_3 + 2\text{HO}$; $857.2 + 225$, or $68.69 + 18$.—This salt precipitates as a bulky and gritty powder, when sulphuric acid is added to a soluble salt of lime. Sulphate of lime appears to have nearly the same degree of solubility at all temperatures, and requires 461 parts of water for solution. It occurs in nature in well-formed crystals, and also in large crystalline masses, forming beds of gypsum; a mineral which contains 2 eq. of water, and of which the density is 2.322 (Roget and Dumas). Mr. Johnston has likewise obtained small prismatic crystals of sulphate of lime, deposited in a steam boiler, which contain only half an equivalent of water (page 330). Sulphate of lime occurs in a crystalline form, without water, forming the mineral *anhydrite*, of which the density is about 2.96. Sulphate of lime fuses at a strong red heat, without decomposition, and on cooling assumes the crystalline form of the last mineral. To form plaster of Paris, gypsum, in pieces about the size of a pigeon's egg, is heated in an oven till it is nearly anhydrous, and then reduced to powder. When this is made into a paste with a little water, it forms a hard coherent mass, or sets, in a minute or two, with a slight evolution of heat. This artificial hydrate, or *stucco*, has the same composition as native gypsum. If sulphate of lime has been heated above 300° , in drying, it refuses to set when mixed with water.

Hyposulphite of lime is formed by adding sulphurous acid to a solution of sulphuret of calcium, till the solution is neutral and colourless. The solution is decomposed when heated above 140° (60° cent.) into sulphur and sulphite of lime. If evapo-

rated below that temperature, it yields large hexagonal prisms of hyposulphite of lime, on cooling, which are colourless. They contain 5 eq. of water, and are persistent in air.

Nitrate of lime is a highly deliquescent salt, which crystallizes with 6 eq. of water, like the nitrates of the magnesian class. It is soluble in alcohol.

Phosphates of lime.—When earth of bones is dissolved in hydrochloric acid, and the solution afterwards neutralised by ammonia, that substance is thrown down as a light gelatinous precipitate, which Berzelius has distinguished as the bone-earth phosphate. It contains 8 eq. of lime, with 3 eq. of phosphoric acid. When moderately dried, it retains, I find, 4 eq. of water; and as it is a tribasic phosphate, its formula probably is $2(3\text{CaO}, \text{PO}_5) + \text{HO}, 2\text{CaO}, \text{PO}_5 + 3\text{HO}$.

On adding chloride of calcium to the tribasic subphosphate of soda, a corresponding phosphate of lime precipitates, of which the formula is $3\text{CaO}, \text{PO}_5$. This phosphate occurs in nature in combination with fluoride of calcium in the form of hexagonal prisms, in the minerals *apatite* and *moroxite*. The formula of apatite is $\text{CaF} + 3(3\text{CaO}, \text{PO}_5)$. The native phosphates of lead occur in the same form, with chloride of lead in the place of fluoride of calcium. *Hedyphan* is the same mineral, in which a portion of phosphoric acid is replaced by arsenic acid.

Another tribasic phosphate of lime is obtained on pouring the solution of common phosphate of soda, drop by drop, into chloride of calcium; the liquid becomes acid. This precipitate is slightly crystalline. Its formula, exclusive of its water of crystallization, is $\text{HO}, 2\text{CaO}, \text{PO}_5$. Berzelius describes also a bi-phosphate of lime, obtained on evaporating a solution of the preceding salt in nitric acid to the point of crystallization, of which the probable formula is $2\text{HO}, \text{CaO}, \text{PO}_5$. There also exist a pyrophosphate and metaphosphate of lime. The insoluble phosphates of lime are soluble in water containing carbonic acid. It is possibly in this manner that phosphate of lime is dissolved by the alkaline animal fluids.

Chloride of lime, bleaching powder.—This compound is equally remarkable for its valuable applications in the arts, and for the discussions to which its anomalous or doubtful constitution has given rise. It is generally prepared by exposing hydrate of lime, from the purest lime, to chlorine gas, the latter being sup-

plied so gradually as to prevent the heat, occasioned by the combination, from rising above 62° . When dried at 212° , hydrate of lime, I find, absorbs afterwards little or no chlorine; but dried over sulphuric acid, without heat, it is, on the contrary, in the most favourable condition for making chloride of lime. A dry, white, pulverulent compound is obtained, by exposing the last hydrate to chlorine, which contains 41.2 or 41.4 chlorine, in 100 parts; but of this chlorine about 39 parts only are available for bleaching, owing to 2 parts of that element going to the formation of chloride of calcium and chlorate of lime. A slight addition of moisture to hydrate of lime does not increase the proportion of chlorine absorbed, and renders the compound less stable. The above appears to be the maximum absorption of chlorine by dry hydrate of lime, and is greater than it would be advisable to attempt in the manufacture of bleaching powder, owing to the occurrence of the partial decomposition adverted to. Yet this proportion is considerably short of 1 eq. of chlorine to 1 of hydrate of lime, which are 48.57 chlorine and 51.43 hydrate of lime, in 100 parts. The excess of lime appears to be useful in adding to the stability of the compound. The bleaching powder of commerce may contain, when newly prepared, about 30 per cent of chlorine. As I have found it in the shops of the apothecaries, the proportion of available chlorine was more frequently below than above 10 per cent, so much does it deteriorate by keeping.

The same compound is obtained in solution by transmitting a stream of chlorine gas through hydrate of lime suspended in water. The lime then absorbs a full equivalent of chlorine, and dissolves entirely. Ten parts of water take up the bleaching combination from one part of dry chloride of lime, leaving undissolved the hydrate of lime contained in excess. The solution has a strong alkaline reaction. It destroys most organic matters containing hydrogen, including colouring matters. But its bleaching action is not instantaneous, unless an acid be added to it, which liberates the chlorine. Hence when Turkey-red cloth, having a pattern printed upon it with tartaric acid thickened by gum, is immersed for about one minute in this solution, it comes out with the colour discharged where the acid was present, but elsewhere uninjured. In this manner white figures are produced upon a coloured ground. The solution of chloride of lime also absorbs and destroys contagious matters in the atmosphere, and is slowly decomposed by carbonic acid, with es-

cape of chlorine. The powder or its solution, when heated, or when kept for a considerable time, undergoes decomposition; 18 eq. of chlorine, then leaving 17 eq. of chloride of calcium, and 1 eq. of chlorate of lime, and disengaging 12 eq. of oxygen gas, according to the observations of M. Morin.

CONSTITUTION OF CHLORIDE OF LIME.

Chloride of lime for bleaching was first prepared by the late Mr. Tennant of Glasgow, who in conjunction with some scientific friends, obtained a patent for the manufacture of the dry compound in 1799. For some time after the true nature of chlorine was known, bleaching powder appears to have been looked upon as simply a combination of chlorine with lime. But more accurate views of combination lead Berzelius to question the possibility of compounds of elementary bodies with binary compounds, which, if they exist, are certainly exceedingly rare, and to observe the similarity in the absorption of chlorine by lime, with its absorption by a strong solution of potash and the formation of chloric acid, and with the solution of sulphur in alkalies and formation of hyposulphurous acid. He concluded that a *chlorous acid* existed in the bleaching compounds of chlorine, consisting of 1 eq. of chlorine and 3 of oxygen; the oxygen of this acid being derived from the metallic oxide like that of chloric and hyposulphurous acids, a corresponding quantity of metallic chloride being produced at the same time. This opinion was generally received, the bleaching power of the compound being referred to the facility with which chlorite of lime parts with 4 eq. of oxygen, and becomes chloride of calcium. The subsequent discovery by M. Balard, of hypochlorous acid, a bleaching compound of chlorine and oxygen, which can be isolated, lent support to the same view, although it altered the expression of it, hypochlorous acid being substituted in these compounds for the chlorous, of the separate existence of which there is no evidence. Hypochlorous acid is actually absorbed by hydrate of lime and by solutions of alkalies, with the formation of bleaching compounds, but the identity of these with the compounds resulting from the absorption of chlorine itself is doubtful. The hypochlorous compounds are much less stable than the old chlorides, according to the observations of M. Martens*.

* Ann. de Ch. et de Ph. t. 61, p. 293.

M. E. Millon has quite recently announced some curious discoveries respecting these compounds, which lead him to take a new and simpler view of their constitution. When the solution of chloride of lime is added to nitrate of lead, a white precipitate falls, which after a time becomes brown. In the first state it has hitherto been taken for chloride, and in the second for peroxide of lead, but Millon finds that it is a compound of protoxide of lead with chlorine, in both conditions, or $Pb + O, Cl$. With protonitrate of iron, a brown precipitate, of similar constitution, $Fe_2 + O_2, Cl$ is produced; and with proto-salts of manganese a similar precipitate, but containing twice as much chlorine. In the case of each of these three nitrates, the new compound corresponds with the peroxide of the same metal, the protoxide acquiring chlorine instead of oxygen. The red oxide, or suboxide of copper also, when warmed, absorbs half an equivalent of chlorine, becoming $2Cu + O, Cl$, which corresponds with the black oxide, the highest degree of oxidation of that metal. Potash, he finds also, to absorb 2 equivalents of chlorine, forming a compound $K + O, 2Cl$, corresponding with the peroxide of potassium, KO_3 ; while soda absorbs only 1 eq. of chlorine, forming $Na + O, Cl$; the peroxide of sodium containing less oxygen than the peroxide of potassium, although the composition of the former appears not to be certainly determined. M. Millon concludes that the compounds formed when chlorine is absorbed by metallic protoxides are bodies analogous to the peroxides of the same metals, but in which the place of a portion of the oxygen is held by chlorine. Bleaching powder is thus a compound of calcium with oxygen and chlorine, in a hydrated condition, analogous to hydrated peroxide of calcium, or hydrated peroxide of barium which is better known. As a peroxide of hydrogen exists, the possibility is inferred of an analogous compound of hydrogen with oxygen and chlorine, $H + O, Cl$, which may be contained in the crystalline compound hitherto viewed as a hydrate of chlorine*. We have already admitted similar substitutions of chlorine for oxygen, as in chlorosulphuric acid (page 332). The relation between a hydrated peroxide, such as that of barium, and chloride of lime appears, in both being decomposed by acids, which unite with the barytes and lime, and liberate oxygen from the one compound and chlorine from the other. Peroxide of hydrogen also

* Journal de Pharmacie, Sept. 1839, page 595.

rivals the chlorine compounds in bleaching power. But when the replacing bodies differ so much from each other as chlorine and oxygen, it is not to be expected that the resulting compounds will exhibit the closest analogy in properties.

CHLORIMETRY.

The bleaching power of chloride of lime is often estimated by the quantity of a solution of sulphate of indigo, which a known weight of chloride can discolour or render yellow. But as the indigo solution alters by keeping, this method is not unobjectionable. Several exact methods have been proposed, of which that in which sulphate of iron is used appears to be entitled to preference. This method reposes upon the circumstance that the chlorine of chloride of lime converts a salt of the protoxide into a salt of the peroxide of iron; half an equivalent, or 221.3 parts of chlorine, effecting that change upon a whole equivalent, or 1728 parts of *cr.* protosulphate of iron. Protoxide of iron is convertible into peroxide by half an equivalent of oxygen, which the half equivalent of chlorine may be supposed to supply, by decomposing water, in becoming hydrochloric acid. It follows, by proportion, that 10 grains of chlorine are capable of peroxidising 78.1 grains of *cr.* sulphate of iron.

A few ounces of good crystals of protosulphate of iron are reduced to powder, and dried by strong pressure between folds of cloth; the salt may afterwards be preserved in a bottle without change. In a chlorimetric experiment 78 grains (equivalent to 10 grains of chlorine) of this salt are dissolved in about two ounces of water, which may be acidulated by a few drops of sulphuric or hydrochloric acid. Fifty grains of the chloride of lime to be examined are dissolved in about two ounces of tepid water, by rubbing them together in a mortar, and the whole poured into the alkalimeter (page 466); which is afterwards filled up to 0 on the scale, by the addition of water, and the whole mixed by inverting the alkalimeter upon the palm of the hand. The solution of chloride of lime, being thus made up to 100 measures, is poured gradually into the sulphate of iron, till the latter is completely peroxidised, and the number of measures of chloride required to produce that effect observed. The change in the degree of oxidation of the iron solution is discovered by means of red prussiate of potash, which gives a precipitate of prussian blue with a salt of the

protoxide of iron only, and not with a salt of the peroxide. By means of a glass stirrer, a white stoneware plate is spotted over with small drops of the prussiate. A drop of the iron solution is mixed with one of these, after every addition of chloride of lime, and the additions continued, so long as a deep blue precipitate is produced. The liquid may continue to be coloured green by the iron salt, but that is of no moment. The richer the specimen of chloride of lime is in chlorine, the fewer measures of its solution are required to peroxidise the iron, the number of measures containing 10 grains of chlorine always producing that effect. The quantity of chlorine in the fifty grains of bleaching powder is now known, being ascertained by the proportion, as m measures (the number poured out of the alkalimeter) is to 10 grains of chlorine, so 100 is to the total grains of chlorine. In a particular experiment the 78 grains of sulphate of iron required 72 measures of the bleaching solution. Hence, as 72 is to 10, so 100 is to 13.89 chlorine in 50 grains of the chloride of lime. The quantity of chlorine in 100 grains of the chloride, or the per centage of chlorine, is obtained by doubling that number, and was therefore in this instance 27.78 per cent, or 28 per cent. The arithmetical process may always be reduced to that of dividing 2000 by the number of measures poured from the alkalimeter; thus in the last example—

$$\frac{2000}{72} = 27.78.$$

SECTION VII.

MAGNESIUM.

Eq. 158.3, or 12.69; Mg.

To obtain magnesium, sodium in a test-tube of hard glass is covered by fragments of anhydrous chloride of magnesium, and heated to redness by a lamp. The alkaline metal unites with chlorine, with strong ignition. After extracting the chloride of sodium by means of water, the magnesium remains in little globules, which may be re-united, by fusing them under a stratum of chloride of potassium at a moderate red heat.

Magnesium has the colour and lustre of silver; it is malleable,

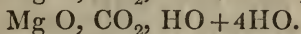
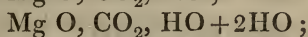
and fuses at a red heat. It is oxidised superficially by moist air, but undergoes no change in dry air or oxygen. Heated to redness, it burns with great brilliancy, forming magnesia. It is evidently more analogous to zinc than to the preceding metals.

Magnesia ; Mg O ; 258.3, or 20.69.—This is the only known oxide of magnesium. As usually prepared by calcining the artificial carbonate of magnesia, it forms the *magnesia usta* of pharmacy. Magnesia is a white soft powder, of density about 2.3, and highly infusible. It combines with water, but with much less avidity than lime, forming a protohydrate. The native hydrate of magnesia has the same composition, and so has the compound, obtained by precipitating magnesia from its soluble salts, when dried, either without heat, or at 212° . These preparations have a silky lustre and a softness to the touch, characteristic of magnesian minerals, such as is observed in asbestos and soapstone. According to Dr. Fyfe, magnesia requires, for solution, 5142 times its weight of water at 60° , and 36,000 times its weight of boiling water. This earth, when mixed with a blue infusion of cabbage, causes it to become green, and is therefore alkaline.

Chloride of magnesium, made by neutralising carbonate of magnesia with hydrochloric acid, crystallizes with 6HO , is very soluble and highly deliquescent. When we attempt to make it anhydrous by heat, hydrochloric acid escapes, and magnesia remains. But the pure chloride, which is employed in preparing the metal, may be obtained by dividing a quantity of hydrochloric acid into two equal portions, neutralising one with magnesia, and the other with ammonia, mixing and evaporating these two solutions to dryness, when an anhydrous double chloride of magnesium and ammonia is formed. On heating this salt to redness in a porcelain crucible, sal-ammoniac sublimes, and chloride of magnesium remains in a state of fusion, which becomes a translucent crystalline mass on cooling. This chloride is decomposed by oxygen, which, at a high temperature, displaces its chlorine, and magnesia is formed.

Carbonate of magnesia.—This salt occurs native, generally as a white, hard, compact mineral of an earthy fracture, which is known as *magnesite*, and sometimes in rhombohedral crystals, similar to those of carbonate of lime. It is prepared artificially by precipitating a soluble salt of magnesia, by means of carbo-

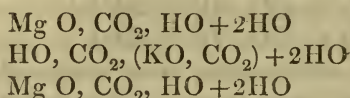
nate of potash at the boiling point. The precipitate is diffused in pure water, and a stream of carbonic acid sent through it, by which the carbonate of magnesia is dissolved. On allowing this solution to evaporate spontaneously the excess of carbonic acid escapes, and carbonate of magnesia is deposited in small hexagonal prisms with right summits. These crystals contain 3 eq. of water. They effloresce in dry air, and then lose 2 eq. of water, according to my own observations. Carbonate of magnesia has also been obtained in crystals with 5 eq. of water. There are, consequently, three hydrates of this salt, of which the formulæ are, $\text{Mg O, CO}_2, \text{HO}$;



The fact that this salt dissolves in carbonic acid water is not to be held as proof of the existence of a bicarbonate of magnesia. Various insoluble salts, such as phosphate of lime and fluoride of calcium dissolve in the same liquid, which appears to possess a specific solvent power. In the analogous solution of carbonate of lime in carbonic acid water, the proportion of the carbonate was found by Berthollet to have a variable and indefinite relation to the acid. On theoretical grounds, supersalts of magnesia, or the magnesian family of oxides, of the ordinary constitution, are not to be expected, as they would be double salts of water and another magnesian oxide.

Magnesia alba, or the subcarbonate of magnesia of pharmacy, is prepared by precipitating a boiling solution of sulphate of magnesia or chloride of magnesium, by means of carbonate of potash. Carbonate of soda is not so suitable as a precipitant of magnesia, as a portion of it is apt to go down in combination with the magnesian carbonate, but it may be used provided the quantity applied be less than is required to decompose the whole magnesian salt in solution. *Magnesia alba*, when well washed with hot water is very white, light and bulky. A portion of carbonic acid is lost, the magnesia not being in combination with a full equivalent of that acid. Berzelius found *magnesia alba* to contain, in 100 parts, 35.77 carbonic acid, 44.75 magnesia, and 19.48 water, or to consist of 3 eq. of carbonic acid, 4 eq. of magnesia, and 4 eq. of water. He views it as a combination of hydrate of magnesia with hydrated carbonate of magnesia, of which the formula is $\text{Mg O, HO} + 3(\text{Mg O, CO}_2, \text{HO})$. This compound is said to require 2493 parts of cold, and 9000 of hot water for solution.

Bicarbonate of potash and magnesia.—This salt was formed by Berzelius by mixing a solution of nitrate of magnesia or chloride of magnesium, with a saturated solution of bicarbonate of potash in excess, and allowing the liquor to rest. In the course of a few days, the double salt is deposited in large regular crystals. These crystals are insipid. They are insoluble in pure water, but are slowly decomposed by it. The composition of this salt corresponds with 1 eq. of potash, 2 of magnesia, 4 of carbonic acid, and 9 of water. As a compound of 1 eq. of bicarbonate of potash and 2 of carbonate of magnesia, it may be represented thus :—



But a compound like this, of three salts of similar constitution, is not easily reconciled with the ordinary laws of saline combination. This salt loses 8HO, at 212°, or all its combined water, except the single basic equivalent. A corresponding bicarbonate of soda and magnesia also exists.

Dolomite, a magnesian lime-stone, very extensively diffused in nature, is a mixture or combination of the carbonates of lime and magnesia, having the crystalline form of calc-spar. The two salts are almost always in the proportion of single equivalents. It is remarkable that when this rock is exposed to the solvent action of water containing carbonic acid, the carbonate of lime is dissolved exclusively, and a magnesian limestone remains in the form of a porous and crystalline mass. It is not unusual to find whole mountains of magnesian limestone thus altered.

Sulphate of magnesia ; $\text{Mg O, SO}_3, \text{HO} + 6\text{HO}$; 759.6 + 787.5, or 60.86 + 63.—This salt exists in many mineral springs, in the waters of Epsom, of Seidlitz in Bohemia, &c., from which it was first procured by evaporation. It is now generally obtained from the bittern of sea water, which consists principally of chloride of magnesium and sulphate of magnesia, and is converted wholly into sulphate by the addition of sulphuric acid. Or magnesia is precipitated from seawater confined in a tank, by means of hydrate of lime, and the earth thus obtained, afterwards neutralised by sulphuric acid. Magnesian limestone is also had recourse to for magnesia. It is burnt and slaked with water, to obtain it in a divided state, and then neutralised by

sulphuric acid. The mixt sulphates are easily separated, that of lime being soluble to a small extent only, while that of magnesia is highly soluble in water. A solution of sulphate of lime is also decomposed by carbonate of magnesia, with the formation of sulphate of magnesia, and this reaction is often witnessed in beds of magnesian limestone, when water containing sulphate of lime, percolates through them.

The crystals of sulphate of magnesia are four-sided rectangular prisms, which when pure, have a slight disposition to effloresce in dry air. One hundred parts of water at 32° dissolve 25.76 parts of the anhydrous salt, and for every degree above that temperature, they take up 0.26564 part additional, (see Gay-Lussac's table of the solubility of salts, at page 182). The solution has a bitter disagreeable taste, which is characteristic of all the soluble salts of magnesia. It is not precipitated in the cold by the alkaline bicarbonates, by common carbonate of ammonia, nor by oxalate of ammonia if the solution of sulphate of magnesia be dilute.

Sulphate of magnesia loses 6HO considerably under 300° , but retains 1 eq. even at 400° . The last equivalent is replaced by sulphate of potash, forming the double sulphate of magnesia and potash, which is considerably less soluble than the sulphate of magnesia, and crystallizes with 6HO . Sulphate of magnesia unites directly with sulphate of ammonia also, when solutions of the salts are used, but not with sulphate of soda. A double sulphate of magnesia and soda occurs, however, in the manufacture of sulphate of magnesia, which is said to have 6HO , like the potash salt, but a different form.

Sulphate of magnesia, when ignited in contact with charcoal, leaves a sulphuret of the metal, but it is the last of the earths which exhibits this analogy to the alkalies. The sulphuret of magnesium is soluble in water. It may likewise be obtained by precipitating sulphate of magnesia by sulphuret of barium.

Hyposulphate of magnesia forms crystals, which are persistent in air, very soluble, and contain 36.77 per cent, or 6 atoms of water of crystallization, like the following salt.

Nitrate of magnesia is a very soluble and highly deliquescent salt. It crystallizes with 6HO , five of which it loses at a high temperature. The remaining hydrate may be fused without decomposition, but when heated more strongly, it loses both nitric acid and water, and pure magnesia is left. It appears

that one equivalent of water is essential to the existence of this and all other nitrates of the magnesian class of oxides. That water is not displaced by nitrate of potash heated in contact with the magnesian nitrate. Nitrate of magnesia is very soluble in alcohol, and forms a solid alcoate, in which probably a portion of water is associated with the alcohol. I did not succeed in forming a double nitrate of magnesia and ammonia, (nor any other double nitrate), although such a salt is admitted by Berzelius.

Phosphate of magnesia is formed on mixing cold solutions of common phosphate of soda and of sulphate of magnesia, and allowing the liquid to stand for 24 hours. The salt appears in tufts of slender prisms, which effloresce in dry air. They are soluble in about 1000 times their weight of water. The composition of this salt, which I carefully examined, may be expressed by the following formula, $\text{HO}, 2\text{Mg O}, \text{PO}_5 + 2\text{HO} + 12\text{HO}$. (Phil. Trans. 1837.)

Phosphate of magnesia and ammonia.—This is the well-known granular precipitate, which appears, when a tribasic phosphate and a salt of ammonia are dissolved together, and any salt of magnesia is added to the mixture. Its formation is had recourse to as a test of the presence of magnesia. Although insoluble in a liquid containing salts, it is so soluble in pure water that it cannot be washed without sensible loss. It is readily dissolved by acids. The same substance forms the basis of the variety of urinary calculus, known as the ammoniaco-magnesian phosphate. It is a tribasic phosphate, of which the 3 atoms of base are 1 atom of oxide of ammonium and 2 atoms of magnesia, with 12 atoms of water of crystallization; ten of the latter may be expelled without any loss of ammonia. The formula of this salt is therefore $\text{NH}_4 \text{O}, 2\text{Mg O}, \text{PO}_5 + 2\text{HO} + 10\text{HO}$. Dr. Otto has observed a corresponding tribasic phosphate of protoxide of iron and ammonia, which contains only two atoms of water of crystallization; and also an arseniate of manganese and ammonia, of which the water of crystallization appears to be the same as that of the phosphate of magnesia and ammonia.

Borate of magnesia.—The neutral salt was obtained by Wöhler, in the form of crystals, by heating a mixture of the solutions of sulphate of magnesia and borax to the boiling point, to form a precipitate, and allowing the liquid to digest for

some time upon this precipitate, at a temperature only a few degrees above 32° . The precipitate re-dissolves, and there are formed on the sides of the vessel thin crystalline needles, transparent, brilliant, hard, and having much of a mineral character. They are insoluble in hot or cold water. They lose by heat 58.4 per cent of water, or 8 atoms, and leave a compound of single equivalents of boracic acid and magnesia, $\text{Mg O}, \text{BO}_3$. After the deposition of this neutral borate, the liquid affords large crystals of a double borate of soda and magnesia, containing 52.5 per cent of water, but of which the proportions of the constituent salts have not been determined.

The mineral *boracite*, which occurs in the cube and its allied forms, is an anhydrous compound of magnesia and boracic acid, in the extraordinary ratio of 3 eq. of magnesia to 4 of boracic acid, or its formula is $3\text{Mg O} + 4\text{BO}_3$. This mineral becomes electrical by heat. The rare mineral, *hydroboracite*, is, according to Hess, a compound of a borate of lime and borate of magnesia, in both of which the acid and base are in the same ratio as in boracite, with 18 eq. of water.

Silicates of magnesia.—Magnesia is found combined with silicic acid in various proportions, forming several mineral species, of which the formulæ are as follows:—

Steatite . . . $\text{Mg O}, \text{Si O}_3$.

Meerschaum . . . $\text{Mg O}, \text{Si O}_3 + \text{HO}$.

Picrosmine and pyrallo-
lite . . . } $3\text{Mg O} + 2\text{Si O}_3$.

Periote (olivine, or chrysolyte) . . . } $3\text{Mg O} + \text{Si O}_3$.

Serpentine (hydrate of
magnesia with subsilicate of magnesia) . . . } $3\text{Mg O}, 6\text{HO} + 2(3\text{Mg O} + 2\text{Si O}_3)$.

Pyroxene or augite (silicate of lime and magnesia) . . . } $3\text{Ca O}, 2\text{Si O}_3 + 3\text{Mg O}, 2\text{Si O}_3$.

Amphibole, or hornblende (silicate of lime and magnesia) . . . } $\text{Ca O}, \text{Si O}_3 + 3\text{Mg O}, 2\text{Si O}_3$.

In these minerals, particularly the two last, the magnesia is often replaced in whole or in part by protoxide of iron, which gives them a green, and sometimes black colour. Fine crystals of pyroxene are often found among the scorïæ of blast furnaces. Serpentine is easily decomposed by acids, and may be employed in the preparation of sulphate of magnesia.

ORDER III.

METALLIC BASES OF THE EARTHS.

SECTION VIII.

ALUMINUM.

Eq. 171.2, or 13.72; Al.

This element is named from *alumen*, the Latin term for alum, which is a double salt, consisting of sulphate of alumina and sulphate of potash.

Like the preceding metal, aluminum is obtained from its chloride, by the action of potassium. But the decomposition must be effected in a platinum or porcelain crucible, as the heat evolved from the reaction, which occurs, would fuse glass. Eight or 10 grains of potassium are covered by a quantity of anhydrous chloride of aluminum, containing, as nearly as possible, the proportion of chlorine equivalent to the potassium; the lid of the crucible is fastened down by a wire, and the heat of a lamp applied. The action which follows is violent, and attended with the evolution of much heat. The aluminum is afterwards separated from the chloride of potassium, with which it is mixt, by digesting the crucible and its contents in a considerable quantity of cold water. The metal appears as a grey powder, resembling spongy platinum, but is seen in a strong light, while suspended in water, to consist of small scales or spangles having the metallic lustre. It is not a conductor of electricity when in this divided state, but becomes one when its particles are approximated by fusion. Wöhler finds that iron resembles aluminum in that respect.

Aluminum has no action upon water at the usual temperature, but decomposes it to a small extent, at the boiling temperature, with the evolution of hydrogen. It undergoes oxidation more rapidly in solutions of potash, soda and ammonia, and the resulting alumina is dissolved by these alkalies. Aluminum requires for fusion a temperature higher than that at which cast iron melts. Heated in open air it takes fire and burns with a vivid light, and in oxygen gas with the production of so much heat as to fuse the alumina, which then has a yel-

lowish colour, and is equal in hardness to the native crystallized aluminous earth, corundum.

Alumina; Al_2O_3 ; 642.4, or 51.44.—This earth is the only degree of oxidation of which aluminum is susceptible, so far as is known at present. In its constitution, alumina is presumed to resemble peroxide of iron, because it occurs crystallized in the same form as the native peroxide of iron, and the salts, into which it enters, are strictly isomorphous with the corresponding salts of that oxide. To three atoms of oxygen it must, therefore, contain two atoms of metal, such being the composition of peroxide of iron. Aluminum is not known to enter into any other combination in a less proportion than two equivalents.

Alumina occurs in a state of purity, with the exception of a trace of colouring matter, in two precious stones, the *sapphire* and *ruby*, the first of which is blue, and the other red. They are not inferior in hardness to the diamond. Their density is from 3.9 to 3.97. It may be obtained by calcining the sulphate of alumina and ammonia, or ammoniacal alum, very strongly. But alumina so prepared is insoluble in acids. It is obtained in the state of a hydrate from common alum, by dissolving the latter in boiling water, and adding a solution of carbonate of potash till it no longer causes a precipitate; a slight excess of the carbonate may then be added, and the whole allowed to digest at a gentle heat for some time, in order to decompose a subsulphate of alumina which the alkali first throws down. The precipitate, which is white, gelatinous, and very bulky, must be carefully washed, by mixing it several times with a large quantity of distilled water, allowing it to settle and pouring off the clear liquid, or by affusion and decantation, as it is said. The precipitate is then dissolved in hydrochloric acid, the solution filtered, if not clear, and precipitated again by ammonia or its carbonate. This last operation is necessary, in order to get rid of a portion of carbonate of potash which remains attached to alumina, when precipitated by that salt. Ammonia cannot be substituted for potash in the first precipitation, as it throws down a subsulphate of alumina, and does not deprive the earth entirely of its acid. The alumina of the second precipitation is also in the state of a subsalt, unless ammonia be added in excess, which is capable of decomposing completely the subsalt from hydrochloric acid. The alumina

must again be carefully washed, as before, to get rid of every portion of the liquid in which it was precipitated. By drying in air, alumina is reduced to a few hundredths of the bulk of the humid mass. It is still a hydrate, but when ignited at a high temperature, it gives pure alumina. One hundred parts of alum furnish only 10.3 parts of alumina.

Alumina is white and friable. It has no taste, but adheres to the tongue. Before the oxihydrogen blow-pipe, it melts into a colourless glass. After being ignited, it is dissolved by acids with great difficulty. It is highly hygrometric, condensing about 15 per cent of moisture from the atmosphere in damp weather. If ignited alumina contains a small portion of magnesia, it becomes warm when moistened with water; this property is very sensible, even when the proportion of magnesia does not exceed half a per cent. It appears to be due to heat disengaged by humectation, a phenomenon first observed by Pouillet.

The hydrate of alumina, when moist, is gelatinous and semi-transparent, like starch, but dries up into gummy masses. It is completely insoluble in water, but is readily dissolved by acids, and also by the fixed alkalis. Caustic ammonia dissolves it, only in very small quantity. When an excess of the hydrate, immediately after precipitation, is digested in caustic potash, by a moderate temperature, and the solution filtered and sealed up in a flask, there separate from it after a time crystals upon the sides of the vessel. The same crystals are obtained, on allowing the solution to absorb carbonic acid slowly from the air. They are white and transparent at the edges, and contain 34.61 per cent of water, or 3 equivalents, which they do not lose at 212° . (Mitscherlich's *Traité*.) The mineral *gibbsite* is a native hydrate of alumina of the same composition, $\text{Al}_2\text{O}_3 + 3\text{HO}$. Another native hydrate exists, containing less water, $\text{Al}_2\text{O}_3 + 2\text{HO}$. It is called *diaspor* by mineralogists, from decrepitating and falling to powder when heated, a property which the artificial hydrate in gummy masses likewise exhibits.

Hydrated alumina has a peculiar attraction for organic matter, which it withdraws from solution, and hence this earth is apt to be discoloured when washed with water not absolutely pure. This affinity is so strong, that when digested in solutions of vegetable colouring matters, alumina combines with, and carries down the colouring matter, which is removed entirely from the

liquid, if the alumina is in sufficient quantity. The pigments called *lakes* are such aluminous compounds. The fibre of cotton, when charged with this earth, attracts and retains with force the same colouring matters. Hence, the great application of aluminous salts in dyeing, to impregnate cloth or yarn with alumina, and thus enable it to fix the colouring matter, and produce a fast colour.

Alumina, it will be observed, is not a protoxide, and is greatly inferior to the preceding earths in basic power. It is dissolved by acids, but never neutralises them completely. Hence, alum and all the salts of alumina have an acid reaction. Their solutions have an astringent and sweetish taste which is peculiar to them. Alumina dissolves, to the extent of several equivalents, in some acids, particularly hydrochloric acid, forming feeble compounds, which are even deprived of a portion of their alumina, by filtering them through paper. It does not combine with some of the weaker acids, such as carbonic acid. Hence an alkaline carbonate throws down alumina from alum, and not a carbonate of that earth. Alumina dissolves readily in solutions of potash or soda, forming compounds in which it must play the part of an acid. Such combinations occur in nature, *spinell* being an aluminate of magnesia ($\text{Mg O, Al}_2 \text{O}_3$), and *gahnite* an aluminate of zinc ($\text{Zn O, Al}_2 \text{O}_3$).

All the known compounds of aluminum correspond with alumina, in the ratio of their equivalents, that is, to two atoms of aluminum they contain three atoms of another body.

Sulphuret of aluminum is formed by burning the metal in the vapour of sulphur. It is a black semi-metallic mass, which is rapidly transformed, by contact of water, into alumina and sulphuretted hydrogen. Hydrosulphuret of ammonia has the same effect upon the solution of a salt of alumina, as ammonia itself, neutralising the acid of the salt, and throwing down alumina, while sulphuretted hydrogen escapes.

Chloride of aluminum; $\text{Al}_2 \text{Cl}_3$; 1670.3 or 133.84.—When alumina is dissolved in hydrochloric acid, it is to be supposed that water and a chloride of the metal are formed (3H Cl and $\text{Al}_2 \text{O}_3 = \text{Al}_2 \text{Cl}_3$ and 3HO). The solution, when concentrated by spontaneous evaporation in a very dry atmosphere, yields crystals, which Bonsdorff found to contain 44.7 per cent, or 12 eq. of water. But it generally forms a saline mass, which

deliquesces quickly in the air. When it is attempted to make this salt anhydrous by heat, the chlorine goes off in the form of hydrochloric acid, and pure alumina is left.

The anhydrous chloride was discovered by Oersted, who made known a method of preparing it, which has since had numerous applications. Pure alumina, free from potash, is intimately mixed with carbon, in the form of lampblack, and strongly calcined in a crucible. The alumina is thus made anhydrous, without being otherwise altered. It is then introduced into a porcelain tube, which is placed across a furnace and exposed to a red heat. Chlorine gas, carefully dried, is conducted over the materials in the tube, when, under the conjoint influence of carbon and chlorine the alumina is decomposed; its oxygen is carried off by the carbon as carbonic oxide gas, and chlorine unites with the aluminum itself, in the place of oxygen. The chloride of aluminum, being volatile, sublimes and condenses in the cool part of the porcelain tube. A glass tube, a little smaller than the porcelain tube, should be introduced into this part of the latter, which may afterwards be drawn out, containing the condensed chloride. The salt is partly in the state of long crystalline needles, and partly in the form of a firm and solid mass which is easily detached from the glass.

Chloride of aluminum is of a pale greenish yellow colour, and to a certain degree translucent. In air it fumes slightly, diffuses an odour of hydrochloric acid, and runs into a liquid by the absorption of moisture. It is very soluble in water, but cannot again be recovered in the anhydrous condition. It is equally soluble in alcohol. Chloride of aluminum combines with sulphuretted hydrogen, phosphuretted hydrogen, and also with ammonia. The latter compound Persoz finds to contain 27.61 per cent of ammonia, $=\text{Al}_2\text{Cl}_3 + 3\text{NH}_3$.

The *fluoride of aluminum* can only be obtained by dissolving pure alumina in hydrofluoric acid; it does not crystallize. This fluoride unites in two proportions with fluoride of potassium, for which it has a strong affinity. Both the compounds are gelatinous precipitates, which become white and pulverulent after being washed and dried. Berzelius assigns to them the formulæ, $3\text{KF} + \text{Al}_2\text{F}_3$ and $2\text{KF} + \text{Al}_2\text{F}_3$. Fluoride of aluminum exists in two crystalline minerals, one of which, on account

of its transparency, hardness and brilliancy, is reckoned among the precious stones. They are, with their formulæ after Berzelius :—

Topaz . . . $3(\text{Al}_2\text{O}_3, \text{SiO}_3) + (\text{Al}_2\text{O}_3 + \text{Al}_2\text{F}_3)$

Pykrite . . . $3(\text{Al}_2\text{O}_3, \text{SiO}_3) + \text{Al}_2\text{F}_3$.

The *sulphocyanide of aluminum* crystallizes in octohedrons, which are persistent in air.

SALTS OF ALUMINA.

Sulphate of alumina; $\text{Al}_2\text{O}_3, 3\text{SO}_3 + 18\text{HO}$; 2145.8 + 2024.6, or 171.95 + 162.23.—Obtained by dissolving alumina in sulphuric acid. It crystallizes with difficulty in thin flexible plates of a pearly lustre, has a sweet and astringent taste, and is soluble in twice its weight of cold water, but does not dissolve in alcohol. When heated it fuses in its water of crystallization, swells up, and forms a light porous mass, which appears at first to be insoluble in water, but dissolves completely after a time. Heated to redness it is entirely decomposed; the residue is pure alumina. This salt has been found in the crystalline form, in the volcanic island of Milo in the Archipelago. Sulphuric acid and alumina combine in several proportions, but this is considered the neutral sulphate, as it possesses the same number of atoms of acid, as it contains of atoms of oxygen in the base.

Another sulphate of alumina ($\text{Al}_2\text{O}_3, 3\text{SO}_3 + \text{Al}_2\text{O}_3$) is obtained, according to Maus, by saturating sulphuric acid with alumina, which contains twice as much alumina as the neutral sulphate. After evaporation this subsalt presents itself in a gummy mass, which dissolves in a small quantity of water, but is decomposed when the solution is diluted with a large quantity of water, or boiled; in that case the neutral salt remains in solution, and the following salt precipitates. Subtrisulphate of alumina ($\text{Al}_2\text{O}_3, 3\text{SO}_3 + 2\text{Al}_2\text{O}_3$) precipitates on adding ammonia to the sulphate of alumina, as a white insoluble powder, which is not decomposed by an excess of ammonia. It contains besides 46.9 per cent of water, or 9 atoms. This subsalt forms the mineral *aluminite*, which is found near Newhaven in England, and at Halle in Germany.

Alum, sulphate of alumina and potash; $\text{KO}, \text{SO}_3 + \text{Al}_2\text{O}_3, 3\text{SO}_3 + 24\text{HO}$; 3236.9 + 2700, or 259.38 + 216.—Sulphate of alumina has a strong affinity for sulphate of potash, in conse-

quence of which octohedral crystals of this double salt precipitate, whenever any salt of potash is added to a strong solution of sulphate of alumina. Alum is a salt of which large quantities are consumed in dyeing. It is prepared by several processes, or derived from different sources. It may be prepared by decomposing clay with sulphuric acid; the decomposition is effected in the most complete manner by igniting pure clay, grinding it afterwards to powder and mixing it with 0.45 of sulphuric acid, of 1.45 density. This mixture is heated in a reverberatory furnace till the mass becomes very thick; afterwards left to itself for at least a month, and then treated with water to wash out the sulphate of alumina formed. The addition of sulphate of potash converts the last salt into alum. But the mode of manufacture just described has not been found so advantageous as the following, which alone is practised in this country. A series of beds occur low in many of the coal measures, which contain much bisulphuret of iron. One of these known as alum slate is a siliceous clay, containing a considerable portion of coaly matter, and of the metallic sulphuret in a state of minute division. When this mineral is exposed to air and moisture, it soon exfoliates, from the formation of sulphate of iron, the bisulphuret of iron absorbing oxygen like a pyrophorus. The excess of sulphuric acid formed attacks the other bases present, of which the most considerable is alumina. Aluminous schists often require to be moderately calcined or roasted, before they undergo this change in the atmosphere. The mineral being lixiviated, after a sufficient exposure, affords a solution of sulphate of alumina and protosulphate of iron, from which the latter salt is first separated by crystallization. The subsequent addition of sulphate of potash to the liquor, causes the formation of alum; the chloride of potassium answers the same purpose, and has the advantage over the sulphate that it converts the remaining sulphates of iron into chlorides, which are very soluble, and from which the alum is most easily separated by crystallization. A very pure alum is obtained in the Roman states from *alum-stone*, which is simply heated till sulphurous acid begins to escape from it, and the residue of this calcination treated with water. This mineral contains an insoluble subsulphate of alumina with sulphate of potash. The heating has the effect of separating the excess of alumina, so that a neutral

sulphate of alumina is formed. Alum-stone appears to be continually produced at the Solfatara near Naples, and other volcanic districts, by the joint action of sulphurous acid and oxygen upon trachyte, a volcanic rock composed almost entirely of felspar.

Alum requires 18.4 parts of cold and only 0.75 parts of boiling water to dissolve it, and crystallizes very readily in regular octohedrons, of which the apices are always more or less truncated, from the appearance of faces of the cube. The taste of alum is sweet and astringent, and its action decidedly acid, and it dissolves metals, with evolution of hydrogen, as readily as free sulphuric acid. The crystals effloresce slightly in air, and when heated melt in their water of crystallization, which amounts to 45.5 per cent of their weight or 24 atoms. The fused salt in losing this water, becomes viscid, froths greatly, and forms a light porous mass known as burnt alum.

A pyrophorus is formed from an intimate mixture of 3 parts of alum and 1 of sugar, which are first evaporated to dryness together, and then introduced into a small stoneware bottle, and this placed in a crucible and surrounded with sand. The whole is heated to redness till a blue flame appears at the mouth of the bottle, which is allowed to burn for a few minutes, and the mouth then closed by a stopper of chalk. After cooling, the bottle is found to contain a black powder, which becomes red hot when exposed to air, and catches fire also and burns with peculiar vivacity in oxygen gas. This property appears to depend upon the highly divided state of sulphuret of potassium, which is intermixt with charcoal and sulphate of alumina. A pyrophorus can be produced from the sulphate of potash alone, without the sulphate of alumina, but it does not so certainly succeed.

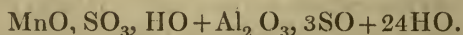
If the quantity of carbonate of soda, necessary to neutralise a portion of alum, be divided into three equal portions, and added in a gradual manner to the aluminous solution, it will be found that the alumina at first precipitated, is redissolved upon stirring, and that no permanent precipitate is produced till nearly two parts of alkaline carbonate are added. It is in the condition of this partially neutralised solution that alum is generally applied as a mordant to cloth. Animal charcoal readily withdraws the excess of alumina from this solution, and so does vegetable

fibre, probably from a similar attraction of surface. When this solution is concentrated by evaporation, alum crystallizes from it, generally in the cubic form, and the excess of alumina is precipitated.

Sulphate of ammonia may be substituted for sulphate of potash in this double salt, giving rise to *ammoniacal alum*, which agrees very closely in properties with potash alum.

Sulphate of alumina also combines with sulphate of soda forming *soda alum*, which crystallizes in the same form as common alum, and also contains 24 HO. Crystals are obtained by mixing the constituent salts, and leaving a concentrated solution to spontaneous evaporation; or by pouring spirits of wine upon the surface of such a solution contained in a bottle, which deposits crystals as the alcohol gradually diffuses through it. This salt effloresces in air, as rapidly as sulphate of soda. It is very soluble in water, 10 parts of water at 60° dissolving 11 parts of this salt.

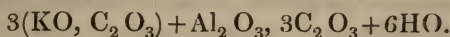
Sulphate of alumina also combines with the sulphate of protoxide of iron, when dissolved with that salt and a considerable admixture of sulphuric acid (Klauer). The double salt was found to contain 1 eq. protosulphate of iron (FeO, SO_3), 1 eq. sulphate of alumina ($\text{Al}_2\text{O}_3, 3\text{SO}_3$), and 24 eq. of water (24HO), which indicates a similarity in composition to alum. But it is deposited in long acicular crystals, which do not belong to the octohedral system, and has therefore no claim to be considered an alum. A similar salt with magnesia was obtained in the same way. Another combination of the same class, containing the sulphate of manganese, forms a white fibrous mineral found in a cave upon Bushman's river in south Africa. This salt has been carefully examined by Apjohn and by Kane, and found to contain 25HO. It is probable that if the proportion of water in Klauer's salts were accurately determined, it would be found to be the same. These salts may be represented as compounds of a magnesian sulphate, retaining its single atom of constitutional water, with sulphate of alumina; the manganese compound thus:—



Certain salts have been formed, isomorphous with alum, and strictly analogous in composition, in which the alumina is re-

placed by metallic oxides isomorphous with it, namely, by peroxide of iron, deutoxide of manganese, and oxide of chromium. To these salts the generic term alum is applied, and the species is distinguished by the name of the metallic peroxide it contains, as *iron alum*, *manganese alum*, and *chrome alum*.

Alumina dissolves freely in most acids, but like metallic peroxides in general, it affords few crystalline salts, except double salts. The oxalate of potash and alumina is the only other of these that has been formed. It is remarkable for its composition, containing 3 eq. oxalate of potash to 1 eq. oxalate of alumina, with 6 eq. of water. Its formula is, therefore,



Like alum it is the type of a genus of double salts. The corresponding oxalates, containing soda, crystallize with 10HO .— (Phil. Trans. 1837, p. 54.)

Nitrate of alumina is said to crystallize with difficulty in prismatic crystals radiating from a centre.

An insoluble *phosphate of alumina* precipitates when phosphate of soda is added to a solution of alum. By fusion it gives a glass like porcelain. Its composition is $2\text{Al}_2\text{O}_3, 3\text{PO}_5$ (Berzelius). This salt, dissolved in an acid and precipitated by ammonia in excess, gives a more highly basic phosphate, of which the formula is $4\text{Al}_2\text{O}_3, 3\text{PO}_5$ (Berzelius). The last salt occurs in nature, in combination with fluoride of aluminum, in the form of radiating crystals, containing 27.8 per cent of water. It is the mineral *wavellite*, of which the formula is $\text{Al}_2\text{F}_3 + 3(4\text{Al}_2\text{O}_3, 3\text{PO}_5) + 36\text{HO}$. A phosphate of alumina and lithia, containing the same subphosphate of alumina, forms the rare mineral *amblygonite*, and may be prepared artificially. Its formula is $2\text{LO}, \text{PO}_5 + 4\text{Al}_2\text{O}_3, 3\text{PO}_5$.

SILICATES OF ALUMINA.

The varieties of *clay* are essentially silicates of alumina, but composed as they are of the insoluble matter of various rocks destroyed by the action of water, it is not to be expected that they will be uniform in composition. Mitscherlich considers it very probable that the basis of clay is usually a subsilicate of alumina, of which the formula is $2\text{Al}_2\text{O}_3, 3\text{SiO}_3$; and which contains 57.42 parts of silica and 42.58 of alumina in 100 parts.

But from the analysis of Mosander, the refractory clay of Stourbridge (a fire-clay) is a neutral silicate of alumina, Al_2O_3 , 3SiO_3 . *China-clay* or *kaolin*, which is prepared from decaying granite, being the result of the decomposition of the felspar and mica of that mineral, is not uniform in its composition.

A subsilicate of alumina exists, forming a very hard crystallized mineral, *disthene* or *cyanite*, of which the formula is $2\text{Al}_2\text{O}_3$, SiO_3 .

Double silicates of alumina and potash are extensively diffused in the mineral kingdom, forming a very considerable portion of the solid crust of the globe. The most usual of these double salts is the following.

Felspar is composed of single equivalents of the neutral silicates of potash and alumina. Its formula is therefore analogous to that of anhydrous alum, silicon being substituted for sulphur; KO , $\text{SiO}_3 + \text{Al}_2\text{O}_3$, 3SiO_3 . It is one of the three principal constituents of granite and gneiss.

Amphigen or *leucite* occurs principally in the lava of Vesuvius in a crystallized state. The relation between the potash and alumina is the same as in the preceding mineral, but it contains one-third less silica. Hence the formula 3KO , $2\text{SiO}_3 + 3(\text{Al}_2\text{O}_3, 2\text{SiO}_3)$. A similar combination is obtained by precipitating a saturated solution of alumina in potash, by a solution of silicate of potash (Berzelius.)

When a mixture of silica and alumina is fused with an excess of potash, and the fused mass washed with water, to withdraw everything soluble, a powder remains in which the potash and alumina are still in the ratio of single equivalents, but in which the oxygen of the silica is equal to that of the bases. This double salt has consequently the formula, 3KO , $\text{SiO}_3 + 3\text{Al}_2\text{O}_3$, 2SiO_3 .

Albite or *soda felspar* much resembles felspar in properties. Its composition is analogous, with the substitution of soda for potash; NaO , $\text{SiO}_3 + \text{Al}_2\text{O}_3$, 3SiO_3 .

Alcalime is the soda silicate proportional to amphigen. It is crystallized like amphigen, but contains 8.27 per cent or 6 atoms of water. Its formula is 3NaO , $2\text{SiO}_3 + 3(\text{Al}_2\text{O}_3, 2\text{SiO}_3) + 6\text{HO}$.

A third compound may be prepared, corresponding with the artificial potash compound above. It occurs also in hexagonal

prisms in the lava of Vesuvius, forming the mineral *nephelin*. Other silicates of soda and alumina are:—

Mesotype or *natrolite*, $\text{NaO}, \text{Si O}_3 + 3(\text{Al}_2 \text{O}_3, \text{Si O}_3) + 2\text{HO}$.

Sodalite, $3\text{NaO}, 2\text{Si O}_3 + 2(\text{Al}_2 \text{O}_3, \text{Si O}_3)$. The latter contains also chlorine.

The two silicates of lithia and alumina are:—

Petalite, $\text{LO}, 2\text{Si O}_3 + \text{Al}_2 \text{O}_3, 3\text{Si O}_3$.

Triphane or *Spodumene*, $\text{LO}, \text{Si O}_3 + \text{Al}_2 \text{O}_3, 2\text{Si O}_3$.

Harmotome is a silicate of barytes and alumina, containing water.

The *silicates of lime and of alumina* combine in many different proportions, forming a great variety of minerals. Most of them contain water, in consequence of which they froth when heated before the blow-pipe, and hence are called *zeolites*. One of these named *stilbite*, from its shining lustre, corresponds in composition with felspar, but contains in addition 6 atoms of water; its formula is $\text{CaO}, \text{Si O}_3 + \text{Al}_2 \text{O}_3, 3\text{Si O}_3 + 6\text{HO}$. A small portion of one or other of the alkalies is often found in these minerals, besides small quantities of protoxide of iron and other magnesian oxides, replacing, it may be presumed, the lime in part. This extensive class of minerals has been very fully studied by Dr. Thomson, who has added considerably to their number.*

Silicate of alumina and magnesia, forms the mineral called *soapstone*, from its resemblance to mottled soap and being unctuous to the touch. The formula assigned to this mineral by Berzelius is $3\text{MgO}, 2\text{Si O}_3 + \text{Al}_2 \text{O}_3, 2\text{Si O}_3 + 6\text{HO}$. The formula of *dichroite*, another combination of the same elements, is $3\text{MgO}, 2\text{Si O}_3 + 3(\text{Al}_2 \text{O}_3, \text{Si O}_3)$.

EARTHENWARE AND PORCELAIN.

The silicate of alumina is the basis of all the varieties of pottery. When moistened with water, clay possesses a high degree of plasticity, and can be extended into the thinnest plates, fashioned into form by the hand, by pressure in moulds; or, when dried to a certain point, be modelled on the turning lathe. It loses its water also in drying, without cracking, provided it is allowed to contract equally in all directions, and acquires greater solidity. When heated more strongly in the potter's kiln, in which it is not fused nor its particles agglu-

* Outlines of Mineralogy and Geology, vol. I.

minated by partial fusion, it becomes a strong solid mass, which adheres to the tongue, and absorbs water with avidity. To render it impermeable by that liquid, it is covered with a vitreous matter, which is fused at a high temperature, and forms an insoluble glaze or varnish upon its surface. But the interior mass of ordinary pottery has always an earthy fracture, and presents no visible trace of fusion.

When an addition is made to the clay, of some compound, which softens or fuses at the temperature at which the earthenware is fired, such as felspar in powder, then the clay is agglutinated by the fusible ingredient, and the mass is rendered semi-transparent, in the same manner as paper that has imbibed melted wax remains translucent after the latter has fixed. The accidental presence of lime, potash, protoxide of iron, or any similar base in the clay, may produce the same effect by forming a fusible silicate diffused through the clay in excess. Such is the constitution of porcelain, and of brown salt-glaze ware of which soda-water bottles are made, which is indeed a sort of porcelain. When these kinds of ware are covered by a fusible material, similar to that which has entered into the composition of their body, and a second time fired, they acquire a vitreous coating. Their fracture is vitreous and not earthy, the broken surface does not adhere to the tongue, and the mass has much greater solidity and strength than the former kinds of earthenware. In combining the ingredients of porcelain, an excess of the fusible ingredient is to be avoided, as it may cause the vessels to soften so much in the kiln as to lose their shape, or even to run down into a glass; while on the other hand if the vitrifiable constituent is in too small a proportion, the heat of the furnace may be inadequate to soften the mass, and to agglutinate it completely.

Porcelain.—The mode of fabricating porcelain, which has been known for a long time to the Chinese, was discovered in 1706 by Böttcher, at Dresden, where the art was first practised in Europe, and published afterwards by Reaumur. The materials employed are (1) a fine and pure clay, prepared by levigation from mouldering granite or other disintegrated felspathic rocks. In China it is called *kaolin*. That consumed in the great potteries of Staffordshire is prepared in Cornwall, and known as China clay. A comparison of compact and disintegrated felspar, shows that by the solvent action of water, the

latter has been deprived of half its silica, and above three-fourths of its potash. The silicate of alumina left, which forms the clay, is very difficult of fusion. The porcelain clay used at Berlin, which is extracted from the decomposed porphyry of Morl, contains, in 100 parts, 71.4 silica, 26 alumina, with small quantities of peroxide of iron, potash, and lime (Mitscherlich).

(2) Pure silica, which is prepared by heating chert or flint to redness, and quenching it in water. The mineral is afterwards obtained, by grinding and subsequent levigation, in a state of the greatest division. The clay and silica, both in the humid state, are then carefully intermixt. A body for the best kind of earthenware may be made of 70 parts of the prepared clay and 24 of ground flint. But to form porcelain an addition is also made (3) of finely levigated felspar, to impart fusibility, the proportion necessary being learned by experiment. Phosphate of lime, sulphate of lime, and carbonate of lime are also added for the same purpose. A mixture of the prepared clay and felspar is also employed, without the introduction of silica. At Berlin, the porcelain earth of Morl is mixed with a quantity of felspar, which, it is said, amounts to about 32 per cent, without the addition of silica. At the royal pottery of Sèvres, in France, the materials employed are felspar as it is found in three different states of decomposition, and which are technically termed *sable cailloteux*, *sable argileux*, and *kaolin*, the last being that in which the decomposition is most advanced, with small quantities of silica (*sable d'Aumont*) and chalk. They are combined in the following proportions:—

Kaolin	70
Sable cailloteux	12
Sable argileux	9.18
Sable d'Aumont	5.29
Lime	3.53 (6.3 chalk.)

100

The body (*pâte*) of the Sèvres porcelain, so formed, consists very uniformly, according to M. Malaguti, in 100 parts, of—

Silica	57 to 58
Alumina	34.5 to 35
Lime	4.5
Potash	3

It forms a highly translucent and beautiful porcelain. Felspar

mixed with a little clay is used as the glaze for this porcelain. Elsewhere a mixture of sulphate of lime, ground porcelain and flint is sometimes used as a glaze. In painting porcelain, the same metallic oxides are employed as in staining glass. They are combined with a vitrifiable material, generally made thin with oil of turpentine, and applied to the pottery sometimes under, and sometimes above the glaze. To fuse the latter colours, the porcelain must be exposed a third time to heat, in the enamel furnace.

Stoneware.—The principal varieties of clay used here, according to Mr. Brande, are the following:—1. *Marly clay*, which, with silica and alumina, contains a portion of carbonate of lime; it is much used in making pale bricks, and as a manure; and when highly heated enters into fusion. 2. *Pipe clay*, which is very plastic and tenacious, and requires a higher temperature than the preceding for fusion; when burned it is of a cream colour, and is used for tobacco-pipes and white pottery. 3. *Potters' clay* is of a reddish or grey colour, and becomes red when heated; it fuses at a bright red heat; mixed with sand it is manufactured into red bricks and tiles, and is also used for coarse pottery (Manual of Chemistry, p. 861). The glaze is applied to articles of ordinary pottery after they are fired, and in the condition of biscuit ware. They are dipped into a mixture of about 60 parts of red lead, 10 of clay, and 20 of ground flint diffused in water to a creamy consistence, and when taken out enough adheres to the piece to give a uniform glazing when again heated. To cover the red colour, which iron gives to the common clays when burnt, the body of the ware is sometimes coloured uniformly of a dull green, by an admixture of oxide of chromium, or made black by oxides of manganese and iron; or oxide of tin is added to the materials of the glaze, to render it white and opaque. The patterns on ordinary earthenware are generally first printed upon tissue paper, in an oily composition, from an engraved plate of copper, and afterwards transferred by applying the paper to the surface of the biscuit ware, to which the colour adheres. The paper is afterwards removed by a wet sponge. The fusion of the colouring matters takes place with that of the glaze, which is subsequently applied, in the second firing. The prevailing colours of these patterns are blue from oxide of cobalt, green from oxide of chromium, and pink from that compound of oxide of tin, lime, and a small quantity of oxide of chromium, known as *pink colour*.

SECTION XI.

GLUCINUM, YTTRIUM, THORIUM, ZIRCONIUM.

GLUCINUM.

Eq. 331.3 or 26.54 ; G.

The compounds of this metal have a considerable analogy to those of aluminum. Glucinum is obtained from its chloride, which is decomposed in the same manner as that of aluminum. This metal is fusible with great difficulty, not oxidable by air or water at the usual temperature, but it takes fire, in oxygen, at a red heat, and burns with a vivid light. It derives its name from *γλυκὺς*, sweet, in allusion to the sweet taste of the salts of its oxide glucina.

Glucina (G_2O_3) is a comparatively rare earth, but is contained to the extent of $13\frac{2}{3}$ per cent in the emerald or beryl, of which specimens that are not transparent or crystallized, can be procured in considerable quantity. To decompose this mineral, which is a silicate of glucina and alumina, it must be reduced to an extremely fine powder, the grosser particles which fall first when the powder is suspended in water, being submitted again to pulverization, and the powder fused with 3 times its weight of carbonate of potash. The calcined mass is moistened with water, and then treated with hydrochloric acid, added in small portions till it is in excess. The potash, alumina and glucina are thus converted into chlorides, and dissolved. The solution is evaporated to dryness on a water-bath, and the residue acidulated by a few drops of hydrochloric acid: the silica remains undissolved. The alumina and glucina are afterwards precipitated together from the solution, by ammonia; and after being well washed, but without being dried, the mixt oxides are digested in a large quantity of carbonate of ammonia, which takes up the glucina without touching the alumina. The liquor is filtered, and the carbonate of ammonia being then expelled from it by ebullition, carbonate of glucina precipitates. The earthy carbonate is ignited, and leaves glucina in the state of a white and light powder, tasteless, infusible, insoluble in water and ammonia, but soluble in potash and soda. Its density is nearly 3. It is distinguished from alumina, by forming a carbonate, and being soluble, when freshly precipitated, in a cold solution of carbonate of ammonia.

Glucina combines with sulphuric acid in several proportions, forming a bisulphate ($2 \text{ G}_2 \text{ O}_3, 6\text{SO}_3$), which is crystallizable, a neutral sulphate ($\text{G}_2 \text{ O}_3, 3\text{SO}_3$), which may be obtained in solution, a soluble subsalt, $\text{G}_2 \text{ O}_3, 2\text{SO}_3$, and an insoluble subsalt, $\text{G}_2 \text{ O}_3, \text{SO}_3$.

Emerald or *beryl* is a silicate of the composition expressed by $\text{G}_2 \text{ O}_3, 4\text{Si O}_3 + 2(\text{Al}_2 \text{ O}_3, 2\text{Si O}_3)$. This mineral crystallizes in six-sided prisms, which are very hard. When coloured green by oxide of chromium it forms the true emerald, and when colourless and transparent *aqua marina*, which are both ranked among the precious stones. The density of the emerald is 2.58 to 2.732.

Euclase is also a silicate of glucina and alumina, $\text{G}_2 \text{ O}_3, 2\text{Si O}_3 + 2(2\text{Al O}_3, \text{Si O}_3)$. It is a very rare mineral, which crystallizes in limpid, greenish prisms.

Chrysoberyl, one of the finest of the gems, consists essentially of 1 atom of glucina combined with 6 atoms of alumina, $\text{G}_2 \text{ O}_3, 6\text{Al}_2 \text{ O}_3$.

YTTRIUM.

Eq. 402.5 or 32.25 ; Y.

The earth yttria was discovered in 1794, by Gadolin, in a mineral from Ytterby in Sweden, which is now called gadolinite. It has since been found in several other minerals, but all of which are exceedingly rare. The metal was isolated from its chloride by Wöhler, precisely in the same manner as the two preceding metals. It is of a darker colour than these metals, and in oxidability resembles glucinum.

Yttria is considered a protoxide, YO. Its density is even greater than barytes, being 4.842. It is absolutely insoluble in the caustic alkalies, is precipitated by yellow prussiate of potash, and its sulphate and some others of its salts have an amethystine tint, properties which distinguish it from the preceding earths.

THORIUM.

Eq. 744.9 or 59.88 ; Th.

This element was discovered by Berzelius, in 1824, in a black mineral, like obsidian, since called *thorite*, from the coast of the North Sea. This mineral contains 57 per cent of thorina. This element has been named from the Scandinavian

deity Thor. The metal was obtained from the chloride, and exhibited a general resemblance to aluminum. Like yttrium, it burns in oxygen with a degree of brilliancy which is quite extraordinary; the resulting oxide does not exhibit the slightest trace of fusion.

Thorina is considered a protoxide, Th O . Its density is 9.402, and therefore superior to that of all other earths. It resembles yttria in being insoluble in alkalies, but differs from that earth in the peculiar property of its sulphate, to be precipitated by ebullition, and to redissolve entirely, although in a slow manner, in cold water. Its sulphate also forms a double salt with sulphate of potash, which dissolves in water, but is insoluble in a liquor saturated with sulphate of potash.

ZIRCONIUM.

Eq. 420.2 or 33.67; Zr.

Zirconium is obtained by heating the double fluoride of zirconium and potassium, with potassium, in a glass or iron tube. On throwing the cooled mass into water, the zirconium remains in the form of a black powder, very like that of charcoal. It contains an admixture of hydrate of zirconia, which may be withdrawn from it by digestion in hydrochloric acid, at 104° (40° cent.) The zirconium is afterwards washed with sal ammoniac to remove completely chloride of zirconium, and then with alcohol to withdraw the sal ammoniac. If washed with pure water, it is apt to pass through the filter. After being thus treated, the powder assumes, under the burnisher, the lustre of iron, and is compressed into scales which resemble graphite. When heated in air it takes fire below redness. It is very slightly attacked by either alkalies or acids, with the exception of hydrofluoric acid, which dissolves it with evolution of hydrogen.

The constitution of *zirconia* is not certainly known, but it is believed to be analogous to that of alumina, $\text{Zr}_2 \text{O}_3$. It was first recognised as a peculiar earth by Klaproth in 1789, who discovered it in the zircon of Ceylon, a silicate of zirconia, which is also found in the syenitic mountains of the south-east side of Norway. The *hyacinth* is the same mineral of a red colour;

it is found in volcanic sand at Expailly in France, in Ceylon, and some other localities. The earth is obtained from this mineral, which is more difficult of decomposition than most others, by processes for which I must refer to Berzelius. (Traité, t. 1, p. 329.)

Zirconia is a white earth, like alumina in appearance, of density 4.3. Its hydrate, after being boiled, is soluble with difficulty in acids. When heated it parts with its water, afterwards glows strongly, from a discharge of heat, becomes denser and less susceptible of being acted on by reagents. It forms a carbonate. When once separated from its combinations, it is insoluble in carbonate of potash or soda, but dissolves in them in the nascent state. The salts of zirconia have a purely astringent taste. It agrees with thorina in being precipitated, when any of its neutral salts are boiled with a solution of sulphate of potash.

ORDER IV.

METALS PROPER HAVING PROTOXIDES ISOMORPHOUS WITH
MAGNESIA, WITH BISMUTH.

SECTION I.

MANGANESE.

Eq. 345.9 or 27.72 ; Mn.

This element is found in the ashes of plants, the bones of animals, and in many minerals, of which that employed in the preparation of oxygen is one of the richest. The black oxide of manganese was long known as *magnesia nigra*, from a fancied relation to *magnesia alba*, but was first thoroughly studied by Scheele in 1774, and by Gahn immediately afterwards, who obtained from it the metal now named manganese.

From its strong affinity for oxygen and the very high temperature which it requires for fusion, manganese is one of the metals proper, which is reduced and fused into a button with

the greatest difficulty. Hydrogen and charcoal, at a red heat, reduce the superior oxides of this metal to the state of protoxide, without eliminating the pure metal at that temperature; but at a white heat, charcoal deprives this metal of its whole oxygen. The following process is recommended by M. John for the reduction of manganese: it illustrates the chief points to be attended to in the reduction of the less tractable metals. Instead of a native oxide, an artificial oxide of manganese, obtained by calcining the carbonate in a well closed vessel, is operated upon. This oxide, which is preferred from being in a high state of division, is mixed with oil and ignited in a covered crucible, so as to convert the oil into charcoal. After several repetitions of this treatment, the carbonaceous mass is reduced to powder, and made into a firm paste by kneading it with a little oil. Finally this paste is introduced into a crucible lined with charcoal (*creuset brasqué*), the unoccupied portion of which is filled up with charcoal powder. The crucible is first heated merely to redness for half an hour, to dry the mass and decompose the oil, after which its cover is carefully luted down, and it is exposed for an hour and a half to the most violent heat of a wind-furnace, that the crucible itself can support without undergoing fusion. The metal is obtained in the form of a semiglobular mass or button in the lower part of the crucible, but not quite pure, as it contains traces of carbon and silicon derived from the ashes of the charcoal. By igniting the metal a second time in a charcoal crucible, with a portion of borax, John obtained it more fusible and brilliant, and so free from charcoal, that it left no black powder when dissolved in an acid.

Manganese is a greyish white metal having the appearance of hard cast iron. Its density according to John is 8.013; while M. Berthier finds it to be 7.05, and Bergman made it 6.850. From its close resemblance to iron, manganese may be expected to be susceptible of magnetism, but its magnetic powers are doubtful. Pecelet has endeavoured to show that manganese can assume and preserve magnetic polarity from the temperature -4° up to 70° , but that it loses it again at higher temperatures. The small difference between the atomic weights of iron, manganese, cobalt and nickel, which are respectively 339.2, 345.9, 369 and 369.9, is remarkable, attended as it is by a great analogy between these metals in many other respects.

Manganese oxidates readily in air, soon falling down as a black powder; in water it occasions a disengagement of hydrogen gas. It is best preserved in naphtha, like potassium, or over mercury. Manganese possesses five degrees of oxidation, with two intermediate or compound oxides.

OXIDES OF MANGANESE.

Protoxide or manganous oxide	Mn O .
Deutoxide or manganic oxide	$\text{Mn}_2 \text{O}_3$.
Peroxide	Mn O_2 .
Red oxide	$\text{Mn}_3 \text{O}_4$, or $\text{Mn O} + \text{Mn}_2 \text{O}_3$.
Varvicite	$\text{Mn}_4 \text{O}_7$, or $\text{Mn}_2 \text{O}_3 + 2\text{Mn O}_2$.
Manganic acid	Mn O_3 .
Hypermanganic acid	$\text{Mn}_2 \text{O}_7$.

Protoxide of manganese, Manganous oxide; Mn O , 445.9 or 35.72.—This is the oxide existing in the ordinary salts of manganese, which are isomorphous with the salts of magnesia. It may be obtained by fusing at a red heat in a platinum crucible, a mixture of equal parts of pure chloride of manganese and carbonate of soda, with a small quantity of sal ammoniac. By the reaction between the first mentioned salts, chloride of sodium is produced and carbonate of manganese, which is decomposed at a red heat, leaving the protoxide of that metal. The hydrogen of the sal ammoniac reduces to the state of protoxide, at the same time, any peroxide which may be formed by absorption of oxygen from the air. Any one of the superior oxides of manganese, in the state of a fine powder, may be converted into protoxide by transmitting hydrogen gas over it, in a porcelain tube at a red heat; the peroxide obtained by igniting the nitrate of the protoxide of manganese is recommended by Dr. Turner as the most easily deoxidated. The protoxide of manganese is a powder of a greyish green colour, more or less deep. When obtained by means of hydrogen at a low temperature, it absorbs oxygen from the air, soon becoming brown throughout its whole mass, and is, indeed, sometimes a pyrophorus; but when prepared by hydrogen at a high temperature, or prepared by means of an alkali, this oxide is permanent. It dissolves readily in acids, and is a strong base. When an alkali is added to a solution of its salts, protoxide of manganese is precipitated white, as a hydrate, which immediately absorbs

oxygen from the air and becomes brown; collected on a filter and washed, it ends by changing into a blackish brown powder, which is the hydrate of the deutoxide. A similar change is instantaneously produced by the action of chlorine-water upon the white hydrate, or by the addition of chloride of lime to a salt of the protoxide of manganese, but then the hydrated peroxide is formed. Protoxide of manganese resembles magnesia and protoxide of iron, in being precipitated by ammonia only in part.

Its salts are sometimes colourless, but more generally of a pale rose tint, which has been ascribed to a trace of manganic acid. But as the rose tint is not destroyed by sulphuretted hydrogen, it must be considered as a peculiar, although only occasional, character of manganous salts, (p. 152). Solutions of the salts of manganese containing a strong acid in excess, are not precipitated by sulphuretted hydrogen.

Protosulphuret of manganese may be procured in the dry way, by heating a mixture of deutoxide of manganese and sulphur. Sulphurous acid is disengaged, and a green powder remains, which dissolves in acids with disengagement of sulphuretted hydrogen. The same compound is obtained in the humid way, when acetate of manganese is decomposed by sulphuretted hydrogen, or a manganous salt precipitated by an alkaline sulphuret. The precipitate is hydrated, and of an orange colour. When the protosulphate of manganese is decomposed by hydrogen at a red heat, it affords an oxisulphuret.

Protochloride of manganese; $\text{MnCl} + 4\text{HO}$; 788.5 + 450 or 63.19 + 36. This salt crystallizes in thick tables, which are oblong and quadrilateral, of a rose colour, is very soluble in water and slightly deliquescent. The residuary liquid in preparing chlorine, by dissolving peroxide of manganese in hydrochloric acid, consists of chloride of manganese contaminated by a portion of perchloride of iron. To remove the latter and obtain a pure chloride of manganese, the solution should be boiled down considerably, to expel the excess of acid, diluted afterwards with water and boiled again with carbonate of manganese, which salt precipitates the whole peroxide of iron, forming chloride of manganese with its acid (Mr. Everitt). If about one fourth of the impure solution of chloride of manganese be reserved, and precipitated by carbonate of soda, a quan-

tity of carbonate of manganese will be obtained, sufficient to precipitate the iron from the other three fourths of the liquid, and which may be used for that purpose after it has been washed. The chloride of manganese, is precipitated white, when free from iron, without any shade of blue, by the ferrocyanide of potassium. The crystals retain one, from their four equivalents of water, at 212° (Brandes), but may be made anhydrous at a higher temperature. Brandes finds 100 parts of water to dissolve at 50° , 38.3; at 88° , 46.2; at 144.5° , 55 parts of the anhydrous salt. A higher temperature instead of increasing the solubility of this salt diminishes it. Absolute alcohol dissolves half its weight of the anhydrous chloride of manganese, and affords by evaporation in vacuo, a crystalline alcoate, containing two equivalents of alcohol.

The corresponding *fluoride of manganese* forms a double salt with fluoride of silicon, which is very soluble in water and crystallizes in long regular prisms of six sides. The formula of this double salt is, after Berzelius, $2\text{Si F}_3 + 3\text{Mn F} + 21\text{HO}$.

Carbonate of manganese is a white insoluble powder, which acquires a brown tint when exposed in the dry state at 140° . It is decomposed by a red heat. Carbonate of manganese occurs in the mineral kingdom, but never in a state of purity, being mixed with the carbonates of lime and iron, which have the same crystalline form. Its presence in spathic carbonate of iron is said to be the cause, why the latter yields an iron peculiarly adapted for the manufacture of steel.

Protosulphate of manganese; $\text{Mn O}, \text{SO}_3 + 7\text{HO}$.—A solution of this salt used in dyeing and entirely free from iron, is prepared by igniting the peroxide of manganese mixed with about one-tenth of its weight of pounded coal, in a gas retort. The protoxide thus formed is dissolved in sulphuric acid, with the addition at the end of a little hydrochloric acid; the sulphate is evaporated to dryness and heated again to redness in the gas retort. The iron is found after ignition in the state of peroxide and insoluble, the persulphate of iron being decomposed, while the sulphate of manganese is not injured by the temperature of ignition and remains soluble. The solution is of an amethystine colour, and does not crystallize readily. When cloth is passed through sulphate of manganese and afterwards through a caustic alkali, protoxide of manganese is precipitated upon it, and rapidly becomes brown in the air, or it is peroxidised at

once by passing the cloth through a solution of chloride of lime. The colour thus produced is called manganese brown.

Crystallized under 42° , the sulphate of manganese gives crystals containing 7HO , which have the same form as sulphate of iron. The crystals which form between 45° and 68° , contain 5HO , and are isomorphous with the sulphate of copper. By a higher temperature, from 68° to 86° , a third set of crystals are obtained, which contain 4HO , their form is a right rhombic prism. The sulphate of iron and other sulphates also assume the same form (Mitscherlich). This salt loses 3HO at 240° , but retains 1 eq. even at 400° , like the other magnesian sulphates. M. Kuhn finds, that when a strong solution of the sulphate of manganese is mixed with sulphuric acid and evaporated by heat, a granular salt is precipitated, which contains only one equivalent of water. This sulphate also forms a double salt with sulphate of potash, which contains 6HO . The anhydrous salt is soluble, according to Brandes, in 2 parts of water at 59° , in 1 part at 122° ; but above the latter term, the salt becomes less soluble. It is insoluble in alcohol.

Hyposulphate of manganese (page 335), is obtained by evaporation as a deliquescent saline mass. The peroxide of manganese used in preparing it, should be previously treated with nitric acid, to dissolve out the hydrated oxide, and be well washed. The *oxalate of manganese*, is a highly insoluble salt. The *acetate* is soluble in $3\frac{1}{2}$ parts of cold water, and also in alcohol. The bitartrate of potash dissolves protoxide of manganese, and forms a very soluble double salt, the *tartrate of potash and manganese*, which can be obtained, although with difficulty, in regular crystals.

Deutoxide of manganese, Manganic oxide; Mn_2O_3 ; 991.8 or 79.44. This oxide is left of a dark brown, almost black colour, when the nitrate of the protoxide is gently ignited. It also occurs crystallized in the mineral kingdom, although rarely; its density is 4.818, and it is named *braunite* as a mineral species. The hydrate of manganic oxide is formed by the oxidation in air of the manganous hydrate. The manganic hydrate also frequently occurs in nature of a black colour, both crystallized and amorphous, and is often mixed with the peroxide of manganese. It constitutes the mineral species *manganite*, of which the density is 4.3 to 4.4, and the formula $\text{Mn}_2\text{O}_3, \text{HO}$. This oxide

colours glass of a red or violet colour. The common violet or purple stained glass, contains manganic oxide; also the amethyst.

Manganic oxide is a base isomorphous with alumina and the peroxide of iron. It dissolves in cold hydrochloric acid, without decomposition, and in sulphuric acid, with a slight digestion. The manganic sulphate was found by Mitscherlich to form an alum, with sulphate of potash. Its solutions have a deep brown colour. At a higher temperature acids reduce the deutoxide of manganese to the state of protoxide, with evolution of oxygen gas.

Sesquichloride of manganese ($\text{Mn}_2 \text{Cl}_3$) is formed when the deutoxide is dissolved in hydrochloric acid at a low temperature. The solution is yellowish brown or black, according to its degree of concentration, and is decomposed by a slight elevation of temperature, with evolution of chlorine. A corresponding *sesquifluoride* may be crystallized.

Sesquicyanide of manganese.—A compound of this cyanide is formed, when the protacetate of manganese is mixed with hydrocyanic acid in excess, then neutralised with potash and evaporated; by the absorption of oxygen, the manganous cyanide is changed into hydrated manganic oxide and manganic cyanide, which last combines with cyanide of potassium, and appears, on the cooling of a concentrated solution, in red crystals, which dissolve easily in water, (Mitscherlich). This salt is analogous to red prussiate of potash, containing manganese instead of iron, and may, therefore, be represented as containing manganicyanogen—a *manganicyanide of potassium*, $\text{K}_3 + (\text{M}_2 \text{Cy}_6)$. As a double cyanide, its formula would be, $3\text{KC}_y + \text{Mn}_2 \text{Cy}_3$.

Red oxide of manganese, MnO , Mn_2O_3 , named by Berzelius manganoso-manganic oxide, is produced at all times when any oxide of manganese is heated strongly in air. It is a double oxide, being a compound of single equivalents of protoxide and deutoxide of manganese. It forms the mineral *hausmanite*, which differs from manganite in having manganous oxide in the place of water. Its density is 4.722. Berthier finds that strong nitric acid dissolves out the protoxide of manganese from the red oxide, and leaves a remarkable hydrate of the peroxide, of which the formula is $4\text{MnO}_2 + \text{HO}$.

Peroxide of manganese, *Black oxide of manganese*; MnO_2 ; 545.9 or 43.72.—This is the familiar ore of manganese em-

ployed in the preparation of oxygen and chlorine. It generally occurs massive, of an earthy appearance, and contaminated with various substances such as peroxide of iron, silica and carbonate of lime; but sometimes of a fibrous texture, consisting of small prisms, radiating from a common centre. Its density varies from 4.819 to 4.94; as a mineral species it has been named *pyrolusite*.* Another important variety of this ore, known as *wad*, is essentially a hydrate, containing 1 eq. of water to 2 eq. of peroxide, according to Dr. Turner. A hydrated peroxide, consisting of single equivalents of its constituents, is formed by precipitating the protosalts of manganese by chloride of lime; and the same compound results from the decomposition of the acids of manganese, when diluted with water or an acid. It is possible that the equivalent of this oxide should be doubled, and that its proper formula is Mn_2O_4 , corresponding with peroxide of chlorine, ClO_4 .

The peroxide of manganese, loses one fourth of its oxygen at a low red heat and is changed into deutoxide; by the effect of a bright red heat it loses more oxygen, and becomes red oxide, the condition into which all the oxides of manganese pass when ignited strongly in the open air. The peroxide does not unite either with acids or with alkalies. When boiled with sulphuric acid it yields oxygen gas and a sulphate of the protoxide. In hydrochloric acid it dissolves with gentle digestion, evolving chlorine gas, and forming protochloride of manganese, (page 357). It is extensively used in the arts for preparing chlorine, and also to preserve glass colourless by its oxidating action. In the last application, it is added to the vitreous materials in a relatively small proportion, and becomes protoxide, which is not a colouring oxide, while as deutoxide it would stain glass purple. At the same time it destroys carbonaceous matter, and converts protoxide of iron, which colours glass green, into peroxide which is less injurious.

The mineral *varvicite* was discovered by Mr. Phillips among some ores of manganese from Hartshill in Warwickshire. It is distinguished from the peroxide by being much harder, having more of a lamellated structure, and by yielding water freely when heated to redness. Its density is 4.531. It may be sup-

* From $\pi\nu\rho$, fire, and $\lambda\nu\omega$, I wash, in allusion to its being employed to discharge the brown and green tints of glass.

posed to consist of 1 eq. of deutoxide, and 2 eq. of peroxide with 1 eq. of water (Dr. Turner); its formula is, therefore, $Mn_2O_3, Mn_2O_4 + HO$.

VALUATION OF PEROXIDE OF MANGANESE.

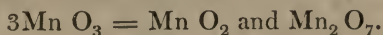
The numerous applications of the higher oxides of manganese depending upon the oxygen which they can furnish, render it important to have the means of estimating expeditiously and without difficulty their value for such purposes. The value of these oxides is exactly proportional to the quantity of chlorine which they produce, when dissolved in hydrochloric acid, and the chlorine can be estimated by the quantity of protosulphate of iron, which it peroxidises. Of pure peroxide of manganese 545.9 parts (1 eq.) produce 442.6 parts of chlorine, which peroxidise 3456 parts (2 eq.) of crystallized protosulphate of iron (page 502). Hence 50 grains of peroxide of manganese yield chlorine sufficient to peroxidise 317 grains (more exactly 316.5 grs.) of protosulphate of iron.

Fifty grains of the powdered oxide of manganese to be examined are weighed out, and also any known quantity, not less than 317 grains, of the sulphate of iron (copperas) employed in chlorimetry. The oxide of manganese is thrown into a flask containing an ounce and a half of strong hydrochloric acid, diluted with half an ounce of water, and a gentle heat applied. The sulphate of iron is gradually added in small quantities to the acid, so as to absorb the chlorine as it is evolved, and the addition of that salt continued till the liquid, after being heated, gives a blue precipitate with the red prussiate of potash, and has no smell of chlorine, which are indications that the protosulphate of iron is present in excess. By weighing what remains of the sulphate of iron, the quantity added is ascertained; say m grains. If the whole manganese were peroxide, it would require 317 grains of sulphate of iron, and that quantity would, therefore, indicate 100 per cent of peroxide in the specimen; but if a portion of the manganese only is peroxide, it will consume a proportionally smaller quantity of the sulphate, which quantity will give the proportion of the peroxide, by the proportion: as 317 : 100 :: m : per centage required. The per centage of peroxide of manganese is thus obtained by multiplying the number of grains of sulphate of iron peroxidised, by 0.317.

It also follows that the per centage of chlorine, which the same specimen of manganese would afford, is obtained by multiplying the number of grains of sulphate of iron peroxidised by 0.2588.

Manganic acid; Mn O_3 ; 645.9 or 51.72.—When peroxide of manganese is strongly ignited with hydrate or carbonate of potash in excess, manganic acid is formed, under the influence of the alkali, together with a lower oxide of manganese. Ignition in open vessels or with an admixture of nitrate of potash, increases the production of the acid, by the absorption of oxygen which then occurs. The product has long been known as *mineral chameleon*, from the property of its solution, which is green at first, to pass rapidly through several shades of colour. But a more convenient process for preparing manganate of potash is that recommended by Dr. Gregory. He mixes intimately 4 parts of peroxide of manganese in fine powder with $3\frac{1}{2}$ parts of chlorate of potash, and adds them to 5 parts of hydrate of potash dissolved in a small quantity of water. The mixture is evaporated to dryness, powdered, and afterwards ignited in a platinum crucible, but not fused, at a low red heat. Digested in a small quantity of cold water, this affords a deep green solution of the alkaline manganate, which may be obtained in crystals of the same colour by evaporating the solution over sulphuric acid in the air-pump. The manganates were discovered by Mitscherlich to be isomorphous with the sulphates and chromates. It has not yet been found possible to isolate manganic acid. Its salts in solution readily undergo decomposition, unless an excess of alkali be present; and are also destroyed by contact of organic matter such as paper.

Hypermanganic acid, Mn_2O_7 ; 1391.8, or 111.44.—When the green solution of manganate of potash, prepared as above directed, is diluted with boiling water, hydrated peroxide of manganese subsides, and the liquid becomes of a beautiful pink or violet colour. The manganic acid is resolved into peroxide of manganese and hypermanganic acid:



The hypermanganate of potash should be rapidly concentrated,

without contact of organic matter, and allowed to crystallize. The crystals are of a dark purple colour, almost black, and soluble in sixteen times their weight of cold water; they were found by Mitscherlich to be isomorphous with hyperchlorate of potash. The hypermanganates give out oxygen when heated, and are reconverted into manganates. Their solutions have a rich purple colour, and are so stable that they may be boiled, if concentrated. A small portion of a hypermanganate imparts a purple colour to a very large quantity of water.

The insoluble manganate of barytes may be formed by fusing peroxide of manganese with nitrate of barytes; and when mixed with a little water, and decomposed by an equivalent quantity of sulphuric acid, affords free hypermanganic acid. In Mitscherlich's experiments, the free acid appeared to be a body not more stable than peroxide of hydrogen, being decomposed between 86° and 104° , with the escape of oxygen gas and precipitation of hydrated peroxide of manganese. It bleached powerfully, and was rapidly destroyed by all kinds of organic matter. M. Huenefeld, on the other hand, obtained hypermanganic acid in a state in which it could be preserved, evaporated, redissolved, &c. He washed the manganate of barytes with hot water, by which it is resolved into peroxide of manganese and hypermanganate of potash, and then added to it the quantity of phosphoric acid exactly necessary to neutralise the barytes. The liberated hypermanganic acid was dissolved out, evaporated to dryness, and by a second solution and evaporation, obtained in the form of a reddish brown mass, crystalline and radiated, which exhibited the lustre of indigo at some points, and was entirely soluble in water. When dry hypermanganic acid was fused in a retort with anhydrous sulphuric acid, and afterwards distilled by a higher temperature, an acicular sublimate, of a crimson red colour was obtained, which appeared to be a combination of hypermanganic and sulphuric acids. (Berzelius's *Traité*, i. 522.)

Hyperchloride of manganese, Mn_2Cl_7 , is a greenish yellow gas, which condenses at zero into a liquid of a greenish brown colour. This liquid diffuses purple fumes, owing to the formation of hydrochloric and hypermanganic acids, by the decomposition of the moisture of the air. It was formed by Dumas by dissolving the manganate of potash in oil of vitriol, pouring

the solution into a tubulated retort, and adding by degrees small portions of fused chloride of sodium or potassium, that is, salt completely free from water. The hyperchloride of manganese is the result of a reaction between the liberated hypermanganic and hydrochloric acids :



A corresponding *hyperfluoride of manganese* was formed by Wöhler by distilling, in a platinum retort, a mixture of manganate of potash and fluor spar in powder, with fuming sulphuric acid. It is a greenish yellow gas, which likewise produces purple fumes in damp air.

ISOMORPHOUS RELATIONS OF MANGANESE.

The compounds of no element enter into so many isomorphous groups, and connect so large a proportion of the elements by the tie of isomorphism as those of manganese. The salts of its protoxide are strictly isomorphous with the salts of magnesia and its class; so that manganese belongs to and represents the magnesian family of elements. The same metal connects the sulphur family with the magnesian, by the isomorphism of the sulphates and manganates; and, therefore, sulphur, selenium, and tellurium are thus allied to the magnesian metals. To these there may be occasion to add oxygen, if the reported discovery, by M. Persoz, of a class of hyposulphites isomorphous with the sulphates should prove to be correct. These hyposulphites are compounds of hyposulphurous acid with basic sulphurets, and present a remarkable analogy, in solubility and other properties, to the sulphates, as well as similarity of form. Being sulphur salts, they are termed sulpho-sulphates by Persoz. The sulpho-sulphate of potash is formed by fusing 80 parts of sulphur with 100 parts of dry carbonate of potash, and washing out the sulphuret of potassium with alcohol.

An equally interesting relation is that of hypermanganic with hyperchloric acid, and the isomorphism, which it establishes, of 2 equivalents of manganese with 1 equivalent of chlorine, and the other members of its family. We are thus

enabled to place together for comparison the corresponding compounds of a magnesian metal or sulphur, and of chlorine, as in the following scheme :

Metallic or Sulphur compound.	Corresponding Chlorine compound.
Suboxide of copper, . Cu_2O	Hypochlorous acid, ClO ,
Manganous oxide, . MnO	Wanting.
Sulphurous acid, . . SO_2	Wanting.
Manganic oxide, . . Mn_2O_3	Wanting.
Manganic acid, . . MnO_3	Wanting.
Peroxide of manganese, Mn_2O_4	Peroxide of chlorine, ClO_4
Hyposulphuric acid, . S_2O_5	Chloric acid, ClO_5 .
Hypermanganic acid, Mn_2O_7	Hyperchloric acid, ClO_7 .

Although hyposulphuric acid is placed in relation with chloric acid, in the preceding table, it is not known that the hypsulphates are isomorphous with the chlorates. It will be observed that the compounds deficient in the chlorine series are the analogues of those containing a single equivalent of manganese or sulphur, and a compound of chlorine and oxygen resembling manganic oxide. The former deficiencies may be connected with the indivisibility of the equivalent of chlorine.

That 2Mn , 2Zn , 2S , 2O , 2H , &c. have the same value and character in combination as Cl , is certainly a very remarkable circumstance. It suggests the idea, that it is by the intimate association or conjunction of *two basyle atoms*, that *one salt-radical atom* is produced ; and consequently that the basyle or salt-radical character of an elementary body is not absolute, but relative to the grouping of its atoms. In discussing the molecular condition of the metallic portions of the voltaic circle, (page 207) it was assumed that the ultimate atoms of a metallic mass are under the influence of chemical affinities, being in a state of chemical combination with one another, and not isolated and independent of each other, like loose grains of sand. The binary or saline structure of the metallic molecule there assumed, may be more precisely described by assigning to it *three* atoms of metal, two of which conjoined form the salt-radical or chlorous atom, and one the basyle or zincous atom. As this molecular theory modifies, in some degree, while it simplifies, and renders greatly

more precise, the view of voltaic action maintained in this work, I shall place in a note below a concise statement of the principles of that view, in its amended form.*

* This modification of the chemical theory of the voltaic circle, which dispenses with any electrical hypothesis, is founded upon the three following postulates :

I. *The binary constitution of salts*, which has already been fully discussed (page 160.) This applies to the fluid portions of the circle, and its assumption is equally necessary on the usually received electro-chemical theory of the circle.

II. *The Sali-molecular structure of metals*.—By this is meant that the metals are composed of molecules or groups of three atoms, having a binary or saline character, as explained above. The metallic and fluid portions of the circle are thus assimilated in constitution. A decomposition can be propagated in any direction through the fluid portion of the circle, owing to the mobility of each particle, which permits it to take the new position required with a change of the direction in which the decomposing force is made to act, (page 204.) But decomposition is propagated, in both directions, through a chain of metallic molecules also, although solid, and therefore without the same power of adjustment. To explain this, it must be supposed that an internal decomposition can readily take place in the metallic molecule itself; that in respect of its three atoms, A, B and C, A forming the zincous element, and B + C the chlorous element, a change can easily occur, in which C becomes the zincous element of the sali-molecule, and A + B the chlorous element; that, supposing the three atoms of the molecules disposed in a line, A, B, C, any of its saline elements may be either to the right or left, as A + BC, or AB + C. The three atoms of the molecule being of one metal, and of the same nature, may admit of this change of internal arrangement, by a substitution of one atom for another.

Several circumstances favour the idea of the existence of the assumed condition of metals: 1. In iron the susceptibility of magnetism is confined to the metal itself and one degree of oxidation, the black oxide, with its corresponding sulphuret. This is the degree of oxidation into which iron most readily passes; it consists of single equivalents of the protoxide and peroxide, or of *three* atoms of iron and four of oxygen. There is oxidation, in its formation, without disturbance of the metallic sali-molecule, $\text{Fe} + \text{Fe}_2$; the zincous element, Fe, combining with 1 eq. of oxygen, to form FeO , and the chlorous element, Fe_2 , with 3 eq. of oxygen, to form Fe_2O_3 ; and these two oxides themselves remaining in a state of union. Metallic iron having, therefore, a common magnetic character with the black oxide of iron, or the loadstone, which has three atoms of metal in its molecule, may well be supposed to have three also. It is worthy of passing remark, that this double oxide is peculiar to the magnetic metals. It may not be an idle hope to look for the elucidation of the cause of magnetism in the peculiarities of the molecular structure of iron.

2. It is supported by the disturbance of chemical affinities, or the electrical

SECTION II.

IRON.

Eg. 339.2 or 27.18; Fe (*ferrum*).

The most remarkable of the metals; the production of which, from the numerous and important applications it possesses, appears to be an indispensable condition of civilization. Meteoric masses of iron, often so pure as to be malleable, are found

effects, consequent upon the contact of different metals; for one metal may be affected by another metal, admitting the reality of their sali-molecular structure, as well as by a salt or acid, the constitution of all these bodies being the same. When copper, for instance, touches zinc, the chlorous element of the copper molecule tends to leave its own zincous element, and to combine with the zincous element of the zinc molecule; so that a similar disturbance takes place as if the zinc were touched by hydrochloric acid. But the phenomena of the contact of metals belong to that class in which the chemical action stops short of combination, the chlorous element of the copper molecule attracting its own zincous element the less that it attracts likewise the zincous element of the zinc, but not abandoning the former and combining with the latter. They belong to the class of the open, and not of the closed circuit. Sulphur, dry acids, peroxides, and many other bodies, disturb the molecular affinities of the metals they touch, in the same manner. The sali-molecule of the highly negative metals, gold, platinum, mercury, &c., contains a strong salt-radical, united with a weak basyle, and resembles hydrochloric acid and the hydrates of the strong acids; while the sali-molecule of the highly positive metals, potassium, zinc, &c., contains a powerful basyle and weak salt-radical, like the hydrated alkalies. In an alloy of two metals, the whole positive metal may exist as basyle, and the negative metal as salt-radical; as in the crystallizable amalgam of cadmium, Cd Hg_2 . The sali-molecule of iron is difficult of decomposition, hence the unusual difficulty of alloying that with other metals, and the tendency of the iron molecule to combine, as a whole, as in the magnetic oxide.

3. The reaction of the sali-molecules of different metals upon each other, when heated, appears to be the cause of the phenomena of thermo-electricity, (page 226), but these are phenomena of the closed circle. It will be evident to those who are acquainted with the Contact Theory of galvanism, so ably developed by Ohm, and supported by the German electricians, and which embraces so happily the whole circle of the phenomena, that the chemical view, advocated here, although founded on a different fundamental assumption, has a more perfect consistency and parallelism in its details with that theory than the electro-chemical theory, generally received, possesses. (Taylor's Scientific Memoirs, No. 7.)

4. The relation of the phosphorus group of elements to the magnesian elements appears to be this: the equivalent of phosphorus, nitrogen, anti-

widely although thinly scattered over the earth's surface, and probably first attracted the attention of mankind to this metal. Of the occurrence of metallic iron as a terrestrial mineral *in situ*, the best established instances are the species of native iron

mony and arsenic is equivalent to *three* magnesian atoms, and yet it is the least combining proportion of the elements enumerated. This view, which was always probable, seems now rendered necessary by the observation of MM. Liebig and Dumas, that in the potash-tartrate of antimony strongly dried, 1 eq. of antimony replaces 3 eq. of hydrogen. Yet the elements of this triple molecule are not separable. In their individual action, however, we appear to have the cause of the singular tendency of the members of the phosphorus family to combine with three equivalents of other bodies, as with 3H, 3O, 3Ni, 3Cu, 3Co, 3Hg, &c., and of the tribasic character of phosphoric, arsenic, and phosphorous acids. These elements, then, have an indissoluble salimolecule. Metallic antimony also is isomorphous with tellurium, and connected, therefore, through sulphur, with the magnesian family.

5. Of the formation of molecular groups of atoms of the same element, apparently united by chemical affinity, it would not be difficult to multiply instances. Thus the atoms of sulphur appear to be associated in a molecular group composed of 12 atoms, when it possesses the crystalline form of bisulphate of potash; for the integrant particle of the salt contains not less than that number of atoms. Supposing also sulphur, in the state of vapour, to be similarly constituted, then, instead of one-third of a volume, its molecule will give four volumes of vapour, the most usual of all proportions. In crystallized sulphur, then, there may exist the same arrangement and aggregation of atoms as in bisulphate of potash, resulting from the action of similar affinities. M. Liebig has represented KS_8 , the pentasulphuret of potassium, by KS_2SS_3 , or as a sort of sulphate of the sulphuret of potassium, which is quite in accordance with these molecular views.

A change in the number of atoms forming the sulphur molecule, or in their arrangement, will account for the dimorphism of that body; indeed, inconsistency of molecular structure may be the general origin of dimorphism. In compound bodies, such as the acids, we have often illustrations of a similar association of several atoms. It appears, in the proportions in which they occasionally unite with bases, as in the terchromate of potash, the teriodate of soda, and may be inferred from the products of their decomposition in other cases. Thus, when chlorate of potash is decomposed by sulphuric acid, *three* equivalents of that salt are decomposed together (page 371), which is certainly a strong presumption that these three equivalents were previously associated in some way, forming one whole. On a similar presumption, Mitscherlich triples the equivalent of white precipitate, and makes it $(3\text{Hg Ad} + 3\text{Hg Cl})$, because that compound affords N Hg_3 as one of the products of its decomposition. It is certainly curious that the aggregation so indicated is very often that of three atoms, as if the atoms of compound bodies affected a salimolecular arrangement, similar to that assumed by the atoms of elements.

III. *The Rotal action of chemical affinity.*—Chemical affinity is certainly capable of acting at a distance in a particular manner. The chemical affinity or

which accompanies the Uralian platinum, and a thin vein about two inches in thickness, observed in chlorite slate, near Canaan in the United States. In a state of combination iron is extensively diffused, being found in small quantity in the soil, and

characteristic attractive power of hydrogen, or of any other basyle, is a constant quantity. When the hydrogen is in combination with chlorine, as hydrochloric acid, that affinity is entirely engrossed by the chlorine. The chemical affinity of the chlorine, on the other hand, which is also a constant quantity, is then entirely engrossed by the hydrogen. But if an atom of zinc Zn, be brought in contact with a particular molecule of hydrochloric acid $\text{Cl} + \text{H}$, then a portion of the affinity of Cl is engaged by Zn, and diverted from H, which is proportionally relieved from that affinity. The unoccupied affinity of H can act upon the Cl' of an adjoining particle of hydrochloric acid; of which the H' , in so far as it is relieved from its own Cl' , can attract the Cl'' of a third particle of hydrochloric acid, and the hydrogen H'' , of this third, the chlorine of a fourth, and thus an action be propagated in a rectilinear direction through the acid to a considerable distance from Zn, where it originated. The unoccupied affinity of the first H, instead of acting upon a single line of particles of hydrochloric acid, as above supposed, may be divided among several lines of particles; these lines will radiate from a common centre Zn, being mutually repulsive of each other, for the same reason as the threads of iron filings attached to the pole of a magnet are so, (page 204). As the number of lines and of particles of acid affected at any particular distance from Zn, will increase with that distance, the action upon any one particle will necessarily diminish with its distance from the disturbing centre Zn, indeed it will be in the inverse ratio of the square of the particle's distance from Zn.

A class of phenomena depending immediately upon the propagation of chemical affinity to a distance are those of *cementation*. When a compact mass of pure iron (a bar of the metal) is exposed to carbonic oxide gas, at a red heat, the superficial particles of iron decompose that gas, by the exertion of a zineous affinity, taking carbon from the oxygen with which it is united, and becoming carburet of iron. But if exposure to the carbonic oxide be continued, the combined carbon does not remain at the surface of the iron, but travels inwards, diffusing itself through the metallic mass. It thus appears that when the iron Fe, of the superficial carburet, which we may represent by $\text{Fe} + \text{C}$ is in contact with a second atom of carbon C' , it attracts C' , and C being proportionally relieved from the affinity of Fe, may act upon the adjoining and interior atom of iron, Fe' , and indeed combine with it, while the external atom Fe combines at the same time with C' . The original atom of carbon C may thus combine in succession with a series of atoms of iron, Fe, Fe' , Fe'' , &c., extending into the interior of the metallic mass, provided always that carbon be constantly supplied to the external atom of iron Fe. Again, the steel may be decarbonised, by exposing it to a source of oxygen, as by heating it in contact with oxide of iron, when the converse of what has been described occurs. The superficial particles of iron being deprived of their carbon, the balance of the attractive forces soliciting that element is turned, and it now travels in an outward direction, and abandons the iron entirely,

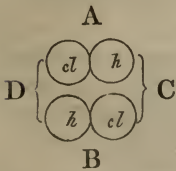
in most minerals, and as sulphuret, oxide and carbonate in quantities which afford an inexhaustible supply of the metal and its preparations, for economical purposes.

Iron differs from any other metal in two points, which

if the external oxidating action is supported for a sufficient length of time. It is very obvious, from the phenomena of cementation, which are exhibited by a great variety of solid bodies besides iron, that a particle of carbon, when in combination with a particle of iron, may still attract and be attracted by the surrounding particles of that metal, and thus exercise an influence at a distance.

The action of chemical affinity described in the preceding cases, as in direction rectilineal, may very readily assume a circular direction or return upon itself. Thus, if two particles of hydrochloric acid, A and B, be disposed to-

FIG. 79.



wards each other, with their unlike atoms together, as in figure 79, it is obvious that, by an inconceivably minute expenditure of force, the *h* of A may be made to unite with the *cl* of B, while the *h* of B combines, at the same time, with the *cl* of A, or the combinations take place indicated by the brackets, and the two new molecules of hydrochloric acid C and D are produced. It is impossible to prove the occurrence of such a decomposition in molecules of the same kind, but we have it constantly

illustrated in double decompositions where the molecules are different—as in hydrochloric acid and cyanide of silver, when the new products, hydrocyanic acid and chloride of silver are formed, and demonstrate its occurrence by a sensible change. Now, instead of a pair of molecules of hydrochloric acid, we may have a circle composed of any number thus in contact, and under-

FIG. 80.



going decomposition, as in the figure. For when the affinity of the *cl* of any acid molecule A (fig. 80) is engaged by *h* of the adjoining molecule B, to its left, the *h* of A is proportionally relieved from the affinity of its own *cl*. The *h* of A is thus free to act upon the *cl* of the acid molecule C to its right; and the relieved hydrogen of that upon the chlorine of a third molecule to the right, and so on round the circle, as indicated by the brackets. When this action reaches B, the *h* of that molecule is thereby relieved

from the attraction of its own *cl*, and on that account can the more readily combine with the *cl* of A.

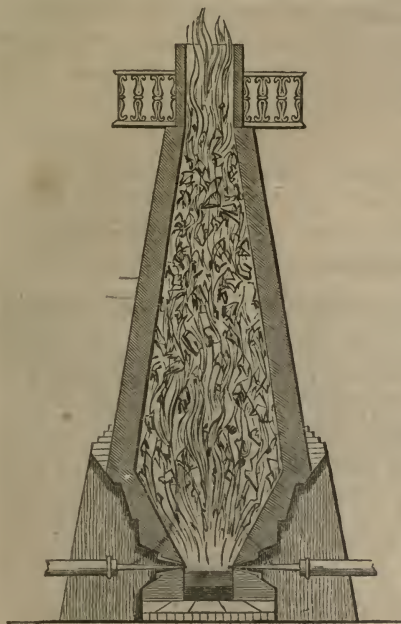
We pass at once from this to the voltaic circle, by supposing that part of these molecules are acid (A), part zinc (B), and part copper (C), but all having the same binary or saline organization, and symmetrically placed in regard to each other. This, which I previously described as the *inductive* action of affinity from its analogy to magnetic induction, I now think may, with more propriety, be distinguished as the *rotal* action of affinity, and founded upon as a fundamental law of chemical affinity. Other applications will be found, for the molecular theory which it involves, in the sequel.

greatly affect the methods of reducing it. Its particles agglutinate at a full red heat, although the pure metal is nearly infusible. The oxides of iron, which are easily reduced by combustible matter, thus yield in the furnace a spongy metallic mass, which may admit of being compacted by subsequent heating and hammering, if the oxide has originally been free from earthy and other foreign matter. Such probably was everywhere the earliest mode of treating the ores of iron, and we find it still followed among rude nations. But iron is also singular in forming, at an elevated temperature, a fusible compound with carbon (cast iron), the production of which facilitates the separation of the metal from every thing extraneous in the ore, and is the basis of the only method of extracting iron, extensively practised.

The ore of iron most abundant in the primary formations, is the black oxide or *magnetic ore*, which affords the most celebrated and valuable irons of Sweden and the north of Europe; but of which the application is greatly circumscribed from its not being associated with coal. In the secondary and tertiary formations, the anhydrous and hydrated peroxide of iron, *red* and *brown hematite*, occur occasionally in considerable quantity, often massive, reniform, and quite pure, at other times pulverulent and mixt with clay. It is employed to some extent in England, in the last condition, but only for the purpose of mixing with the more common ore. The crystallized carbonate of iron, or *spathic iron*, is smelted in some parts of the continent, and gives an iron often remarkable for a large proportion of manganese. The celebrated iron of Elba is derived from *specular* or *oligistic iron*, a crystallized peroxide. But the consumption of all these ores is inconsiderable, compared with that of the *clay iron-stone* of the coal measures. This is the carbonate of the protoxide of iron mixt with variable quantities of clay and carbonates of lime, magnesia, etc.; it is often called the argillaceous carbonate of iron. It is a sedimentary rock wholly without crystallization, resembling a dark coloured limestone, but of higher density, from 2.936 to 3.471, and not effervescing so strongly in an acid. It occurs in strata, beds or bands, as they are also named, from 2 to 10 or 14 inches in thickness, alternating with beds of coal, clay, bituminous schist, and often limestone. The proportion of iron in this ore, varies considerably, but averages about 30 per. cent, and after it has

been calcined, to expel carbonic acid and water about 40 per cent.*

SMELTING CLAY IRON-STONE.



The blast furnace, in which the ore is reduced, is of the form represented in the margin, 55 to 60 feet in height, with an interior diameter of from 14 to 17 feet at the widest part. The cavity of the furnace is entirely filled with fuel, and the other materials, which are continuously supplied from an opening near the top; and the combustion maintained by air thrown in at two or more openings, called *twyeres* near the bottom, under a pressure of about 6 inches of mercury, from a blowing apparatus, so as to maintain the whole contents of the furnace in a

state of intense ignition. When the air to support the combustion has attained a temperature of 600° or 700°, by passing through heated iron tubes, before it is thrown into the furnace, raw coal may be used as the fuel; but with cold air, the coal must be previously charred to expel its volatile matter, and converted into coke, otherwise the heat produced by its combustion is insufficient. With the ore and fuel a third substance is added, generally limestone, the object of which is to form a fusible compound with the earthy matter of the ore; it is, therefore, called a *flux*. Two liquid products accumulate at the bottom of the furnace, namely a glass composed of the flux in combination with the earthy impurities of the ore, which when

* Accurate analyses of several Scotch varieties of this ore have been published by Dr. H. Colquhoun. Brewster's Journal, vii, 234; or Dr. Thomson's Outlines of Mineralogy and Geology, i, 446; and of the French ores by M. Berthier, in his *Traité des Essais par la Voie Sèche*, ii, 252, a work which is quite invaluable for the metallurgic student.

drawn off forms a solid *slag*, and the carburet of iron, or metal, which is the heavier of the two. It may be drawn from observations made by Dr. Clark, in 1833, on the working of the Scotch blast furnaces, under the *hot blast*, that the relative proportions of the materials, including air, and product of cast iron are as follows :*

	Weight.
Coal.	5
Roasted iron stone.	5
Limestone.	1
Air.	11
<hr/>	
Average product of cast iron.	2

The ultimate fixed products are the slag and carburet of iron, but the formation of these is preceded by several interesting changes, which the ore successively undergoes in the course of its descent in the furnace. A portion of the oxide of iron is certainly reduced to the metallic state, soon after its introduction, in the upper part of the furnace, by carbonic oxide and volatile combustible matter ; but the reduced metal does not then fuse. A large portion of the oxide of iron must combine also, at the same time, with the silica and alumina present in the ore, which act as acids, and a glass be formed, of which the oxide of iron is scarcely reducible by carbon. But this injurious effect of the acid earths is counteracted by the lime of the flux, which being a more powerful base than oxide of iron, liberates that oxide from the glass, and neutralises the silica ; so that the slag eventually becomes a silicate of lime and alumina, with scarcely a trace of oxide of iron, when the proportions of the materials introduced into the furnace are properly adjusted. The whole oxide of iron comes thus to be exposed to the reducing action of the volatile combustible, and consequently the whole iron is probably, at one time, in the condition of pure or malleable iron. But when the metal descends somewhat farther in the furnace, it attains the high temperature, at which it combines with the carbon of the coke in contact with it, and it fuses for the first time, in the form of carburet of iron. It has not yet, however, attained its ultimate condition. When it reaches, in its descent, the region of the

* Edinburgh Phil. Trans. vol. 13.

furnace where the heat is most intense, its carbon reacts on the silica, alumina, lime and other alkaline oxides contained in the fluid slag, with which it is accompanied, reducing portions of silicon, aluminum, calcium and other alkaline metals, which combine with the iron. The proportion of carbon replaced by silicon and metallic bases, is generally found to be greater in iron prepared by the hot than by the cold blast, owing, it is presumed, to the higher temperature of the furnace with the hot blast.

The introduction of air already heated to support the combustion of the blast furnace, for which a patent was obtained by Mr. J. B. Neilson, has greatly reduced the proportion of coal required to smelt a given weight of ore, enabling the iron master indeed, to effect a saving of more than three fourths of the coal where that is of a bituminous quality. The air is heated between the blowing apparatus and the furnace, by being made to circulate through a set of arched tubes of moderate diameter, heated by a fire beneath them. The air can be heated in this manner to low redness, or to near 1000° , but there is found to be no proportional advantage in raising its temperature much above the melting point of lead (612°), which is already higher than the point at which charcoal inflames. Considering the great weight of air that enters the furnace, the temperature of that material must greatly affect the whole temperature of the furnace, particularly of the lower part, where the air is admitted, and which part it is desirable should be hottest. Now a certain elevated temperature is [required for the proper smelting of the ore, and unless attained in the furnace, the fuel is consumed to no purpose. The removal of the negative influence of the low temperature of the air, appears to permit the heat to rise to the proper point, which otherwise is attained with difficulty and by a wasteful consumption of fuel. Professor Reich of Freiburg, has observed that heating the air likewise alters the relative temperatures of different parts of the furnace, depressing in particular, and bringing nearer the twyeres, the zone of highest temperature. The admixture of steam with the air has, he finds, precisely the opposite effect, elevating the zone of highest temperature in the furnace; so that the effect of the hot blast, may be exactly neutralised by mixing steam with the hot air.

Cast iron.—The fused metal is run into channels formed in

sand, and thus cast into ingots or pigs, as they are called. Cast iron is an exceedingly variable mixture of reduced substances, of which the principal is iron combined with carbon. The theoretical constitution to which that variety of it, most definite in its composition, approaches, is the following :

WHITE CAST IRON.

Four atoms iron.	94.7
One atom carbon.	5.3
					<hr/>
					100.0

The difference in appearance and quality of the varieties of cast iron is not well accounted for by their composition. The grey or mottled cast iron, forming the qualities, Nos. 1 and 2, presents a fracture composed of small crystals, is easily cut by the file, and is preferred for castings. It is generally supposed that a portion of uncombined carbon is diffused through the iron of these qualities, in the form of graphite. No. 3, or white cast iron is more homogeneous ; its fracture exhibits crystalline plates, like that of antimony, and is nearly white ; it is exceedingly hard and brittle.

Malleable iron.—The great proportion of cast iron manufactured is afterwards refined, or converted into bar or malleable iron. Previous to refining, the cast iron is always fused, and cooled suddenly by throwing water on the melted surface, by which it becomes white cast iron, if not so before. In this condition it is most easily deprived of its carbon, which is the object of the refining. The principal operation, called the puddling process, consists in heating masses of the iron in a kind of reverberatory furnace, with a certain access of air. The metal fuses, and by means of a sort of spatula is stirred about, and every part of it exposed to the flame. The carbon is thus gradually burnt out, partly by the direct action of oxygen in the flame, and partly by cementation with oxide of iron ; and the metal becomes less fusible, but thick and tenacious, so that it sticks together, and is formed into a ball. In this condition it is removed by tongs, compressed into a cylindrical form by a few blows of a loaded hammer, and quickly converted into a bar, by pressing it between grooved rollers. The tenacity of the metal is increased by welding several bars together ; a pile of bars is brought to a full red heat in an

oblong furnace, and then extended between the grooved rollers into a single bar. The texture of malleable iron is fibrous. Although the purest commercial form of the metal, it still contains about one-half per cent of carbon, with traces of silicon and other metals.

Steel.—Only the best qualities of malleable iron, those prepared from a pure ore, and reduced by means of charcoal, such as the Swedish iron, are converted in steel. An iron box is filled with flat bars of such iron and charcoal powder, in alternate layers, and kept at a red heat for forty-eight hours, or longer. The surface of the bars is found afterwards to be blistered, and they have absorbed from 1.3 to 1.75 per cent of carbon. This is the process of cementation, to which allusion has already been made (Note, page 545). It is known that iron can be converted into steel without being in actual contact with charcoal, provided the iron and charcoal are in a close vessel together, and oxygen be present; the carbon reaching the surface of the metal in the form of carbonic oxide gas. The iron becomes harder by this change, and more fusible, but can still be hammered into shape, and cut with a file. The property in which steel differs most from soft iron, is the capacity it has required of becoming excessively hard and elastic, when heated to redness and suddenly cooled by plunging it in water or oil. This hardness makes it invaluable for files, knives, and all kinds of cutting instruments. But the steel, when hardened in the manner described, is harder than is required for most of its applications, and also very brittle. Any portion of its original softness can be restored to the steel by heating it up to particular temperatures, which are judged of by the colour of the film of oxide upon its surface, which passes from pale yellow at about 430° , through straw yellow, brown yellow, and red purple into a deep blue at 580° , and allowing the steel afterwards to cool slowly. Articles of steel are *tempered* in this manner.

Properties of iron.—Iron is of a bluish white colour, and admits of a high polish. It is remarkably malleable, particularly at a high temperature, and of great tenacity. Its mean density is 7.7, which is increased by fusion to 7.8439. When kept for a considerable time at a red heat, its particles often form large cubic or octohedral crystals, and the metal becomes brittle. Malleable iron softens before entering into fusion, and in this

state it can be *welded*, or two pieces be united by hammering them together. The point of fusion of cast iron is 3479° ; that of malleable iron is much higher. Iron expands in becoming solid, and therefore takes the impression of a mould with exactness. Iron is attracted by the magnet at all temperatures under an orange red heat. It is then itself magnetic by induction, but immediately loses its polarity, if pure, when withdrawn from the magnet. If it contains carbon, as steel and cast iron, it is affected less strongly, but more durably, by the proximity of a magnet, becoming then permanently magnetic. The black oxide, which forms the loadstone, and the corresponding sulphuret, are the only compounds of iron which share this property with the metal. A steel magnet loses its polarity at the boiling point of almond oil; a loadstone, just below visible ignition (Faraday).

Iron reduced from the oxide by hydrogen at a heat under redness, forms a spongy mass, which takes fire spontaneously at the usual temperature, when exposed to air, and oxide of iron is reproduced (Magnus). But iron, in mass, appears to undergo no change in dry air, and to be incapable of decomposing pure water at that temperature. Nor does it appear to be acted upon by oxygen and water together, but the presence of carbonic acid in the water, causes the iron to be rapidly oxidated with evolution of hydrogen gas. In the ordinary rusting of iron, the carbonate of the protoxide appears to be first produced, but that gradually passes into the hydrated peroxide, and the carbonic acid is evolved. The rust always contains ammonia, of which the hydrogen is imagined to come from the water decomposed; the native oxides of iron also contain ammonia. Iron remains bright in solutions of the alkalies and in lime-water, which appear to protect it from oxidation, but neutral and more particularly acid salts have the opposite effect. The corrosion of iron under water appears, in general, to be immediately occasioned by the formation of a subsalt of that metal with excess of oxide, of which the acid is supplied by the saline matter in solution. Articles of iron may be completely defended from the injury occasioned in this way, by contact with the more positive metal zinc, as in galvanized iron (page 219); while the protecting metal itself wastes away very slowly. Cast iron is converted into a species of graphite, by many years

immersion in sea-water, the greater part of the iron being dissolved while the carbon remains*. In open air, iron burns at a high temperature with vivacity, and its surface becomes covered with a fused oxide, which may afterwards be detached from it in scales, and forms smithy ashes. Iron also decomposes steam at a red heat, and the same oxide is formed as by the combustion of the metal in air, namely the magnetic or black oxide, $\text{FeO} + \text{Fe}_2\text{O}_3$.

Iron dissolves readily in diluted acids, by substitution for hydrogen, which is evolved as gas. Strong nitric acts violently upon iron, yielding oxygen to it, and undergoing decomposition. But the relations of iron to that acid, when slightly diluted, are exceedingly singular. They have been particularly studied by Professor Schœnbein.

Passive condition of iron.—Pure malleable iron, such as a piece of clean stocking wire, usually dissolves in nitric acid of sp. gr. 1.3 to 1.35, with effervescence, but it may be thrown into a condition in which it is said by Schœnbein to be *passive*, as it is no longer dissolved by that acid, and may be preserved in it for any length of time without change:—1. By oxidating the extremity of the wire slightly, by holding it for a few seconds in the flame of a lamp, and after it is cool, dipping it gradually in the nitric acid, introducing the oxidated end first. 2. By dipping the extremity of the wire once or twice in concentrated nitric acid, and washing it with water. 3. By placing a platinum wire first in the acid, and introducing the iron wire, preserving it in contact with the former, which may afterwards be withdrawn. 4. A fresh iron wire may be introduced in the same manner into the nitric acid, in contact with a wire already passive; this may render passive a third wire, and so on. 5. By making the wire the positive pole or zincoid of a voltaic battery, introducing it after the negative pole or chloroid has been placed in the acid. Oxygen gas is then evolved from the surface of the iron wire, without combining with it, as if the wire were of platinum. As the passive state can be communicated by contact of passive iron, so it may be destroyed by contact with active iron or zinc undergoing, at the moment, solution in the

* Mr. Mallet has collected much information respecting the corrosion of iron, in his First Report to the British Association, on the action of sea and river water upon cast and wrought iron. 1839.

acid. If passive iron be made a negative pole (chlorous) in nitric acid, it also ceases to resist solution. The indifference to chemical action exhibited by iron when passive, is not confined to nitric acid of the density mentioned, but extends to various saline solutions which are usually acted upon by iron. An indifference to nitric acid of the same kind can also be acquired by other metals as well as iron, particularly bismuth (Dr. Andrews), but in a much less degree. That the peculiar condition of the iron, which enables it to resist solution in the nitric acid, is of a voltaic nature cannot be doubted, but its exact character is still very imperfectly defined. In the consideration of the subject, the circumstance is not to be overlooked, that iron may, and does dissolve in nitric acid in two different ways:— (1) When directly oxidated by the decomposition of the acid, and (2) by substitution for the hydrogen of the nitrate of water, as the same metal dissolves in oil of vitriol. The first mode of solution is not known to be connected with voltaic action, but the second is so, and should be promoted by rendering the iron positive or zincous; the condition which actually prevents all solution, and makes iron passive in nitric acid of 1.3 density. But if the predominating tendency of iron is to dissolve in acid of that strength by direct oxidation, which is very probable, it comes to be a question whether increasing the disposition of the metal to dissolve in the other mode, or by substitution, may not counteract the former tendency, and thereby impede the solution of the metal. The passive condition would then be represented as the result of an antagonism in the two forces which act simultaneously upon the metal.* Schœnbein has observed, however, an action of thin films or pellicles of foreign matter adhering to metallic surfaces, which he thinks, with reason, may be concerned in the phenomenon, and which is interesting independently of that relation. Platinum wire, after being plunged for a few seconds in hydrogen gas, acts as a positive metal, or as if it were zinc, when associated with clean platinum in dilute sulphuric acid. This can be explained only

* Dr. Andrews has indeed drawn the conclusion, from observation, that the ordinary chemical action of a hydrated acid upon the metals which dissolve in it, is in general diminished when the acid is concentrated, by the voltaic association of these metals with such metals as gold, platinum, &c; while on the contrary, it is increased when the acid is diluted.—Trans. of the Royal Irish Academy, 1838; or Becquerel, vol. v, pt. 2, p. 187.

by supposing combination of the hydrogen and platinum, and that the superficial polar molecule of the metal then consists of hydrogen as the external zincous element, and platinum as the chlorous element, resembling the positive amalgam of zinc, in which zinc forms the external zincous atom, and mercury the chlorous atom of the molecule (page 208). This hydrogen must decompose the hydrated sulphuric acid ($H + SO_4$), evolving hydrogen, and cause a train of decompositions from the hydruetted to the clean platinum. The analogy between this voltaic action of hydrogen, and the oxidation of hydrogen gas by spongy platinum, adds to its interest. Again, platinum, gold and silver, by being placed for a few seconds in chlorine, become capable of acting negatively, or are chlorous, when they form a circle with clean platinum in dilute sulphuric acid. Here, also, there must be a compound polar molecule, of which the zincous element is platinum, and the external chlorous element chlorine; and this chlorine must combine with the hydrogen, and evolve the salt-radical of the hydrated acid, thus causing a train of decompositions through the latter. A pellicle of peroxide of lead can be precipitated upon the surface of iron and platinum, and then they become strongly chlorous in a voltaic circle, with nitric acid, like platinum with the film of chlorine above, till the pellicle of peroxide is dissolved off by the acid. Here the excess of oxygen in the peroxide must decompose water, or more likely the hydrated acid present, evolving oxygen or the salt-radical of the acid, when the circuit is completed. In such circles, we have the affinity of hydrogen, of chlorine, or of oxygen, originating the rotal action, instead of that of a positive metal, as usual.*

PROTOCOMPOUNDS OF IRON.

Protoxide of iron, Ferrous oxide ; FeO ; 439.2 or 35.18.—Iron appears to admit of only two degrees of oxidation, the protoxide and peroxide, which are both basic, and correspond respectively with manganous and manganic oxides. The protoxide is not easily obtained in a dry state, from the avidity with which it absorbs oxygen. It exists in the sulphate and other salts of iron, formed when the metal dissolves in an acid with the

* Schœnbein and Faraday in the Phil. Mag. 3rd Series, vols. 9, 10, 11, 12 and 14.

evolution of hydrogen, and is precipitated as a white hydrate, when potash is added to these salts, which becomes black on boiling, from loss of water. The colour of the white precipitate changes by exposure to air to grey, then to green, bluish black, and finally to an ochrey red, when it is entirely peroxide.

The protoxide of iron is thrown down by alkalies as a hydrate, and by alkaline carbonates as a carbonate, which are white at first, but soon become of a dirty green, and undergo the same subsequent changes from oxidation. Its salts are not precipitated by sulphuretted hydrogen, the sulphuret of iron being dissolved by strong acids, but give a black sulphuret with solutions of alkaline sulphurets. They give a white precipitate with the ferrocyanide of potassium, which gradually becomes of a deep blue when exposed to air; with the ferricyanide, a precipitate which is at once of an intense blue, being one of the varieties of Prussian blue. The infusion of gall-nuts does not affect a solution of the protoxide of iron when completely free from peroxide.

Protosulphuret of iron is prepared by heating to redness, in a covered crucible, a mixture of iron filings and crude sulphur, in the proportions of 7 of the former and 4 of the latter. It dissolves in sulphuric and hydrochloric acids with evolution of sulphuretted hydrogen gas (page 402).

A *subsulphuret of iron*, Fe_2S , appears to be formed when the sulphate of iron is reduced by hydrogen; one-half of the sulphur coming off in the form of sulphurous acid. This subsulphuret will correspond with the subsulphurets of copper and lead, which crystallize in octohedrons.

Protochloride of iron crystallizes with 4HO , and is very soluble. Like all the soluble protosalts of iron, it is of a green colour, gives a green solution, and has a great avidity for oxygen.

Protiodide of iron is formed when iodine is digested with water and iron wire, the latter being in excess, and is obtained as a crystalline mass by evaporating to dryness. It has been introduced into medical use by Dr. A. T. Thomson. A piece of iron wire is placed in the solution of this salt, to preserve it from oxidising. The protiodide of iron dissolves a large quantity of iodine, without becoming periodide, as the excess of iodine may be precipitated by starch.

Protocyanide of iron is obtained with the same difficulty

as the protoxide of iron. When cyanide of iron is added to a protosalt of iron, a yellowish red precipitate is formed, which dissolves in an excess of the alkaline cyanide, forming the ferrocyanide of potassium (page 450). A grey precipitate is obtained on distilling the ferrocyanide of ammonium by water, and a white insoluble substance on digesting red prussiate of iron with tated prussian blue in sulphuretted hydrogen water, contained in a well-stopped phial, which, although they differ considerably in properties, have both been looked upon as protocyanide of iron. The most remarkable property of this cyanide is its tendency to combine with other cyanides of all classes, and to form double cyanides, or to enter as a constituent into the salt-radicals ferrocyanogen and ferricyanogen $\text{Cy}_3 \text{Fe}$, and $\text{Cy}_6 \text{Fe}_2$. The two following compounds are obtained when the ferrocyanide and the ferricyanide of potassium are added to a protosalt of iron.

Ferrocyanide of potassium and iron; $3\text{Fe} \cdot \text{K} + 2 (\text{Cy}_3 \text{Fe})$.—The bluish white precipitate which falls on testing a protosalt of iron with the ferrocyanide of potassium or yellow prussiate of potash. Of the four equivalents of potassium contained in two equivalents of the latter salt (page 456), three are replaced by three equivalents of iron in the formation of this precipitate, while the three potassium unite with the former salt-radical of the iron. This salt is represented above as consisting of 2 eq. of ferrocyanogen with 4 eq. of metal ($3\text{Fe} + \text{K}$), ferrocyanogen being bibasic. Exposed to the air it absorbs oxygen, and becomes blue. It then affords ferrocyanide of potassium to water, and after all soluble salts are removed, a compound remains, which Liebig names the *basic sesquiferrocyanide of iron*, and represents by the formula $\text{Fe}_4, 3(\text{Cy}_3 \text{Fe}) + \text{Fe}_2 \text{O}_3$, which corresponds, as will be seen afterwards, with 1 eq. of prussian blue + 1 eq. of peroxide of iron. This basic compound is dissolved entirely by continued washing, and affords a beautiful deep blue solution. The addition of any salt causes the separation of this compound. Its solution may be evaporated to dryness without decomposition.

Ferricyanide of iron, Turnbull's blue; $3\text{Fe} + (\text{Cy}_6 \text{Fe}_2)$.—This is the beautiful blue precipitate that falls on adding the ferricyanide of potassium (red prussiate of potash) to a protosalt of iron. It is formed by the substitution of 3 eq. of iron for the 3 eq. of potassium of the latter salt (page 450). The same

blue precipitate may be obtained by adding to a protosalt of iron, a mixture of yellow prussiate of potash, chloride of soda, and hydrochloric acid. The tint of this blue is lighter and more delicate than that of prussian blue. It is occasionally used by the calico-printer, who mixes it with permuriate of tin, and prints the mixture, which is in a great measure soluble, upon Turkey red cloth, *raising* the blue colour afterwards by passing the cloth through a solution of chloride of lime, containing an excess of lime. The chief object of that operation is indeed different, namely, to discharge the red and produce white patterns, where tartaric acid is printed upon the cloth, but it has also the effect incidentally of precipitating the blue pigment and peroxide of tin together on the cloth, by neutralising the acid of the permuriate of tin. This blue is believed to resist the action of alkalies longer than ordinary prussian blue. Mr. R. C. Campbell observed that the ferricyanide of iron may be distinguished from prussian blue by the circumstance, that when boiled in a solution of yellow prussiate of potash, it affords red prussiate of potash, which dissolves, and a grey insoluble residue of ferrocyanide of iron and ferrocyanide of potassium (Liebig).

Carbonate of iron is obtained on adding carbonate of soda to the protosulphate of iron, as a white or greenish white precipitate, which may be washed and preserved in a humid condition in a close vessel, but cannot be dried without losing carbonic acid and becoming peroxide of iron. It is soluble, like the carbonate of lime, in carbonic acid water, and exists under that form in most natural chalybeates. Carbonate of iron occurs also crystallized in the rhomboidal form of calc spar, forming the mineral *spathic iron*, which generally contains portions of carbonates of lime, magnesia, and manganese. It is generally of a cream colour or black, and its density rarely exceeds 3.8. This anhydrous carbonate does not absorb oxygen from the air. Carbonate of iron is also the basis of clay-iron-stone. There is no carbonate of the peroxide.

Sulphate of iron, Ferrous sulphate, Green vitriol, Copperas; $\text{Fe O, SO}_3, \text{HO} + 6\text{HO}$; $940.4 + 787.5$ or $75.3 + 63$.—This salt may be formed by dissolving iron in sulphuric acid diluted with 4 or 5 times its bulk of water, filtering the solution while hot, and setting it aside to crystallize. But the large quantities of sulphate of iron, consumed in the arts, are prepared simulta-

neously with alum, by the oxidation of iron pyrites, (page 516.)

The commercial salt is in large rhomboidal crystals, from an oblique rhomboidal prism, which effloresce slightly in dry air, and when at all damp, absorb oxygen, and become of a rusty red colour; hence the origin of the French term *couperose* applied to this salt, and corrupted in our language into copperas. If these crystals be crushed and deprived of all hygrometric moisture by strong pressure between folds of cotton cloth or filter paper, they may afterwards be preserved in a bottle without any change from oxidation. Of the 7HO which copperas contains, it loses 6HO at 238°, but retains 1 eq. even at 535°. It can be made, however, perfectly anhydrous, with proper caution, without any appreciable loss of acid. It was observed by Mitscherlich to crystallize at 176°, with 4HO, in a right rhombic prism, like the corresponding sulphate of manganese. When its solution, containing an excess of acid, is evaporated by heat, a saline crust is deposited, which, according to Kuhn, contains 3HO. Another hydrate has also been obtained by dissolving the sulphate in sulphuric acid, which contains 2HO, and has the crystalline form and sparing solubility of gypsum (Mitscherlich). The sulphate of iron appears to form neither acid nor basic salts. One part of copperas requires to dissolve it in the following quantities of water, at the particular temperatures indicated above each quantity, according to the observations of Brandes and Firnhaber :

50° — 59° — 75.2° — 109.4° — 114.8° — 140° — 183.2° — 194° — 212°
1.64 — 1.43 — 0.87 — 0.66 — 0.44 — 0.38 — 0.37 — 0.27 — 0.30

The sulphate of iron undergoes decomposition at a red heat, changes into sulphate of the peroxide, and leaves, after all the acid is expelled, the red peroxide known as colcothar. This sulphate, like all the magnesian sulphates, forms a double salt with sulphate of potash, containing 6HO. A solution of the sulphate of iron absorbs nitric oxide, and becomes quite black; it takes up the gas in the proportion of 9 parts to 100 anhydrous salt, according to Peligot, or one-fourth of an equivalent (page 288).

Protonitrate of iron may be formed by dissolving the protosulphuret of iron in nitric acid, diluted and cold; the solution evaporated in vacuo gives pale green crystals, which are

very soluble. The solution of the neutral salt is decomposed near the boiling temperature, with the evolution of nitric oxide, and the precipitation of a subnitrate of the peroxide in abundance. Iron turnings dissolve in pure nitric acid, and form the same salt, without the evolution of any gas, the water and acid undergoing decomposition, so as to produce ammonia, while they oxidate the iron.

Protacetate of iron is obtained by dissolving the metal or its sulphuret in acetic acid. It forms small green prisms, which decompose very readily in the air.

Tartrate of potash and iron is prepared by boiling bitartrate of potash with half its weight of iron turnings and a small quantity of water. Hydrogen gas is evolved, and a white, granular and sparingly soluble salt is formed, which blackens in air from absorption of oxygen. It is used medicinally. The iron of this salt is not precipitated either by hydrate or carbonate of potash.

The *titanate of iron* occurs in masses of a metallic black, or as black grains in volcanic sand. It crystallizes in the form of peroxide of iron, (page 146), with which it is often mixed. Its formula is FeO, TiO_2 .

PERCOMPOUNDS OF IRON.

Peroxide of iron, Ferric oxide, Fe_2O_3 ; 978.4 or 78.36.—Occurs in great abundance in nature: 1. As *oligistic* or *specular iron*, in crystals derived from a rhomboid very near the cube, which are of a brilliant metallic black and often iridescent. Their powder is red; their density from 5.01 to 5.22. This forms the celebrated Elba ore. 2. As *red hematite*, in fibrous, mamillated, or kidney-shaped masses, of a dull red and very hard, of which the density is from 4.8 to 5.0. This mineral is cut, and forms the burnishers of blood-stone. 3. Also in combination with water, as *brown hematite*, which is much more abundantly diffused than the anhydrous peroxide, the granular variety supplying, according to M. Berthier, more than three-fourths of the iron furnaces in France. Its density is 3.922, its powder brown, with a shade of yellow, and it dissolves readily in acids, which the anhydrous peroxide does not. From analyses of Dr. Thomson and M. Berthier, this mineral occurs with 1 eq. of water, or $\text{HO}, \text{Fe}_2\text{O}_3$, analogous to the magnetic oxide of

iron, Fe O , $\text{Fe}_2 \text{O}_3$.* The hydrated peroxide produced by the oxidation of iron pyrites, of which it retains the form, contains 1 eq. of water, or 10.31 per cent, and that from the oxidation of the carbonate of iron, 3 eq. of water, or 14.71 per cent, to 2 eq. of peroxide, (Mitscherlich, *Lehrbuch*, II. 23, 1840.) The hydrate is the yellow colouring matter of clay, and with silica and clay it forms the varieties of ochre.

When metallic iron is oxidated gradually in a large quantity of water, there forms around it a light precipitate of a bright orange yellow, which is a ferric hydrate, according to Berzelius, and of which the empirical formula is $2\text{Fe}_2 \text{O}_3 + 3\text{HO}$, the usual composition of brown hematite. When iron is oxidated in deep water, it is converted, according to Mr. E. Davy, into the magnetic oxide, which is possibly formed by cementation from the hydrated peroxide. The hydrated peroxide is also obtained, by precipitation from the persalts of the metal, by ammonia and by a hydrated or carbonated alkali; but never pure, as when an insufficient quantity of alkali is added, a subsalt containing acid falls, and when the alkali is added in excess, a portion of it goes down in combination with the peroxide, and cannot be entirely removed by washing. When ammonia is used, the water and excess of the precipitant can be expelled by ignition, and the pure peroxide obtained. The latter is not magnetic, and after ignition dissolves with difficulty in acids. When ignited strongly, it loses oxygen and becomes magnetic.

The peroxide of iron and its compounds are strictly isomorphous with alumina and the compounds of that earth, and remarkably analogous to them in properties. It is a weak base, of which the salts have a strong acid reaction, and are decomposed by all the magnesian carbonates, as well as by the magnesian oxides themselves. The solutions of its salts, which are neutral in composition, have generally a yellow tint, but they are all capable, when rather concentrated, of dissolving a great excess of peroxide and then become red. Very dilute solutions of the neutral salts of peroxide of iron are decomposed by ebullition, and the peroxide entirely precipitated, the acid of the salt then uniting with water as a base, (Scheerer.)

* One of the hydrates, probably this one, occurs very rarely crystallized in very small crystals, derived from the cube or octohedron, (Berthier, *Traité*, II. 225), that is, in the form of the magnetic oxide of iron—a circumstance of great interest, if it is an instance of the isomorphism of hydrogen with iron or a magnesian metal.

Iron is most conveniently distinguished by tests, or precipitated for its quantitative estimation, when in the state of peroxide. The solution of a proto-salt is usually peroxidised by transmitting a current of chlorine through it, or by adding to it, at the boiling point, nitric acid, in small quantities, so long as effervescence is occasioned from the escape of nitric oxide. Alkalies and alkaline carbonates precipitate the peroxide in the state of hydrate. Sulphuretted hydrogen converts a persalt of iron into a protosalt, with precipitation of sulphur. The ferrocyanide of potassium throws down prussian blue, but the ferricyanide has no effect upon a persalt of iron. The sulphocyanide of potassium produces a deep wine-red solution with a persalt of iron, which becomes perfectly colourless when considerably diluted with water, provided the salt of iron is not in great excess. Infusion of nut-galls produces a bluish black precipitate—the basis of common writing ink.

Black or magnetic oxide of iron, Fe O , $\text{Fe}_2 \text{O}_3$, called also the ferroso-ferric oxide, an important ore of iron, is a compound of the two oxides. It crystallizes in the regular octohedron. In this compound, the peroxide of iron may be replaced by alumina and by oxide of chromium, and the protoxide of iron by oxide of zinc, magnesia, and protoxide of manganese, without change of form. It was produced artificially, by Liebig and Wöhler, by mixing the dry protochloride of iron with an excess of carbonate of soda, calcining the mixture in a crucible, and treating the mass with water. The double oxide remains as a black powder, which may be washed and dried without its oxidating farther. The same chemists, by dissolving the black oxide in hydrochloric acid, and precipitating by ammonia, obtained a hydrate of the double oxide. It was attracted by a magnet, even when a flocculent precipitate suspended in water. When ignited and anhydrous, this double oxide is much more magnetic than iron itself.

Sesquisulphuret of iron, or Ferric sulphuret, $\text{Fe}_2 \text{S}_3$, corresponding with the peroxide, may be prepared by pouring, drop by drop, a solution of a persalt of iron, into a solution of an alkaline sulphuret, the last being preserved in excess. At a low red heat, it loses 2-9ths of its sulphur and becomes magnetic pyrites. The common yellow iron pyrites is the *bisulphuret of iron*. It crystallizes in the cube or other forms of the regular system, its density is 4.981. It may be formed artificially by

mixing the protosulphuret with half its weight of sulphur, and distilling in a retort by a temperature short of redness. The metallic sulphuret combines with a quantity of sulphur equal to what it already possesses, and forms a bulky powder of a deep yellow colour and metallic lustre, upon which sulphuric and hydrochloric acids have no action. This sulphuret appears to be of a stable nature, but the lower sulphurets of iron oxidate, when moistened, with great avidity. Stromeier found the native magnetic sulphuret of iron to consist of 100 parts of iron combined with 68 of sulphur; and the sulphuret left on distilling iron with sulphur, at a high temperature, to be of the same composition. It may be viewed as $5\text{Fe S} + \text{Fe}_2\text{S}_3$ (Berzelius.) It is said to be this compound which is almost always formed when sulphuret of iron is prepared.

Perchloride of iron, Fe_2Cl_3 , is formed when iron is burned in an excess of chlorine. It is volatile at a red heat. Its solution, which is used in medicine, is obtained by dissolving the hydrated peroxide of iron in diluted hydrochloric acid. When greatly concentrated, the solution of perchloride of iron yields at one time orange yellow crystalline needles, radiating from a centre, which are $\text{Fe}_2\text{Cl}_3 + 12\text{HO}$; at another time, large dark yellowish red crystals, $\text{Fe}_2\text{Cl}_3 + 5\text{HO}$ (Mitscherlich, Lehrbuch II. 498.) Mixed with sal ammoniac, and evaporated in vacuo, it affords beautiful ruby red octohedral crystals, consisting of 2 eq. of chloride of ammonium, and 1 eq. perchloride of iron, with 2 eq. of water, $\text{Fe}_2\text{Cl}_3, 2\text{N H}_4\text{Cl} + 2\text{HO}$. Of this water, the double salt, I find, loses 1 eq. at 150° , and the other when dried above 300° . There is a similar double salt, containing chloride of potassium, but not so easily formed. The perchloride of iron is soluble both in alcohol and ether. A strong aqueous solution was found by Mr. Phillips to dissolve not less than 4 eq. of freshly precipitated hydrated peroxide of iron, becoming deep red and opaque.

Periodide of iron is formed in similar circumstances as the preceding perchloride.

Percyanide, or sesquicyanide of iron, Fe_2Cy_3 , is unknown in a pure state. A solution of it, which is decomposed by evaporation, is obtained by precipitating the potash of the red prussiate by the fluoride of silicon. It forms a numerous class of double cyanides. A compound of the two cyanides of iron, like the compound oxide, is obtained as a green powder, when

a solution of the yellow prussiate of potash, charged with an excess of chlorine, is heated or exposed to air. The precipitate should be boiled with eight or ten times its weight of concentrated hydrochloric acid, and well washed. Its formula is, $\text{Fe Cy, Fe}_2 \text{ Cy}_3 + 4\text{HO.}^*$

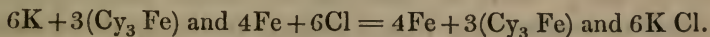
Sesquiferrocyanide of iron, Prussian blue, $\text{Fe}_4, 3(\text{Cy}_3 \text{ Fe})$.—This remarkable substance precipitates whenever the yellow prussiate of potash is added to a persalt of iron. For the preparation of prussian blue in quantity, Liebig recommends the following process of Hochstetter. Six parts of green vitriol and six parts of yellow prussiate of potash to be dissolved, each by itself, in fifteen parts of water, the solutions mixed, and an addition then made to them of one part of oil of vitriol, and twenty four parts of strong hydrochloric acid. After some hours, a clear solution of one part of chloride of lime in eighty parts of water is gradually added, by small portions, observing the precaution to stop as soon as an effervescence is observed, from the disengagement of chlorine. After being allowed to subside for several hours, the precipitate is washed and dried at the usual temperature, or by artificial heat. It is said that the finest colour is obtained by heating the precipitate with dilute nitric acid, till it acquires a deep blue colour, instead of oxidising by chlorine.

Prussian blue, dried at the temperature of the air, is a light porous body, of a rich velvety blue colour; dried at a higher temperature, it is more compact, and exhibits in mass a coppery lustre. It is tasteless, and not poisonous. Alkalies decompose it, precipitating peroxide of iron and reproducing an alkaline ferrocyanide. This renders prussian blue of little value in dyeing, as it is injured by washing with soap. Red oxide of mercury, boiled with prussian blue, affords the soluble cyanide of mercury, with an insoluble mixture of oxide and cyanide of iron. It is destroyed by fuming nitric acid, but combines with oil of vitriol, forming a white pasty mass, which is decomposed by water.

In the formula above, prussian blue is represented as consisting of 4 eq. of iron and 3 eq. of the bibasic salt-radical, ferrocyanogen, and, therefore, named a sesquiferrocyanide. It contains oxygen and hydrogen, besides, which cannot be sepa-

* Pelouze, An. de Ch. et de Ph. t. 69, p. 40.

rated without the decomposition of the compound. In its formation 3 eq. of ferrocyanide of potassium react upon 2 eq. of a persalt of iron. Thus supposing the ferrocyanide of potassium and perchloride of iron to be mixed :



In precipitating prussian blue, care should be taken to avoid an excess of the ferrocyanide of potassium, as the precipitate is apt to carry down a portion of that salt. The combination of prussian blue and peroxide of iron, called *basic prussian blue*, was noticed at page 557.

Although there is no *carbonate of the peroxide of iron*, the hydrated peroxide is dissolved by alkaline bicarbonates, under certain conditions, which are not well understood, and a red solution is formed.

Persulphates of iron.—The neutral persulphate, $Fe_2 O_3, 3SO_3$, is formed by adding to a solution of the protosulphate half as much sulphuric acid as it already contains, and peroxidising by nitric acid. It gives a syrupy liquid, without crystallizing. This salt is found native in Chili, forming a bed of considerable thickness. It is generally massive, but forms also six sided prisms, with right summits, which are colourless, and contain 9HO, (Rose.) The persulphate of iron is soluble in alcohol. It may be made anhydrous by a low red heat; but after ignition dissolves in water with extreme slowness, like calcined alum.

When hydrated peroxide of iron is digested in the neutral sulphate, a red solution is formed, which, according to Maus, is the compound $Fe_2 O_3, 2SO_3$. The rusty precipitate which is formed in a solution of the protosulphate from the absorption of oxygen, is another subsulphate, of which the empirical formula is $SO_3 + 2Fe_2 O_3$.

A double *persulphate of iron and sulphate of potash*, or *iron alum*, is formed by evaporating a solution of the mixed salts to their point of crystallization. It is colourless and quite analogous in composition to ordinary alum, (page 515.) Its formula is $KO, SO_3 + Fe_2 O_3, 3SO_3 + 24HO$.

Another double sulphate is formed, which crystallizes in large six-sided tables, and of which the formula is $2(KO, SO_3) + Fe_2 O_3, 2SO_3 + 6HO$, (Maus), when potash is added gradually to a concentrated solution of persulphate of iron, till the precipitate

formed ceases to redissolve, and the solution is evaporated in vacuo.

Berzelius designates as the *ferroso-ferric sulphate* a combination of the proto and persulphates of iron, $\text{Fe O}, \text{SO}_3 + \text{Fe}_2 \text{O}_3, 3\text{SO}_3$. It is the salt produced when a solution of the neutral protosulphate of iron is exposed to the air, till no more ochre is precipitated. The solution, which is yellowish red, does not crystallize, but gives the black oxide of iron when precipitated by an alkali. A salt of the same constituents, but in different proportions, forms large stalactites, composed of little transparent crystals, in the copper mine of Fahlun. It is represented by $3\text{Fe O}, 2\text{SO}_3 + 3(\text{Fe}_2 \text{O}_3, 2\text{SO}_3) + 36\text{HO}$, (Berzelius.)

Pernitrate of iron.—By dissolving iron in nitric acid, without heat, as in Schœnbein's experiments, (page 553), a salt is obtained in large, transparent, and colourless crystals. From more than one analysis, M. Pelouze found the constituents of this salt to be in the proportion of $2\text{Fe}_2 \text{O}_3 + 3\text{NO}_5 + 1\frac{1}{2}\text{HO}$. Its solution is decomposed by heat, and the peroxide of iron precipitates.

Peroxalate of iron is very soluble and does not crystallize. It forms a double salt with the oxalate of potash, of a rich green colour, of which the formula is $3(\text{KO}, \text{C}_2 \text{O}_3) + \text{Fe}_2 \text{O}_3, 3\text{C}_2 \text{O}_3 + 6\text{HO}$. The crystals effloresce in dry air. In this double salt, the peroxide of iron may be replaced by alumina and oxide of chromium (page 519.) This salt is formed by dissolving the hydrated peroxide of iron to saturation, in binoxalate of potash, (salt of sorrel,) and crystallizes readily from a concentrated solution. The circumstance of its being the salt of peroxide of iron most easily obtained and preserved in a dry state, should recommend it as a pharmaceutical preparation.

The *benzoate and succinate of peroxide of iron* are insoluble precipitates. Hence the benzoate and succinate of ammonia are employed to separate iron from manganese. As both these precipitates are dissolved by acids, the iron solution should be made as neutral as possible. The formula of the succinate is, $\text{Fe}_2 \text{O}_3, \bar{\text{S}}$.

SECTION III.

COBALT.

Eq. 369, or 29.57; Co.

Cobalt occurs in the mineral kingdom chiefly in combination with arsenic, as arsenical cobalt, Co As ; or with sulphur and arsenic, as grey cobalt ore, $\text{Co As} + \text{Co S}_2$, but contaminated with iron, nickel, and other metals. Its name is that of the Kobolds or evil spirits of mines, and was applied to it by the superstitious miners of the middle ages, who were often deceived by the favourable appearance of its ores. These remained without value, till the middle of the sixteenth century, when they were first applied to colour glass blue. They are now consumed in great quantity for the blue colours of porcelain and stoneware. Cobalt is likewise found in almost all meteoric stones.

To obtain metallic cobalt, the native arseniuret is repeatedly roasted, by which the greater part of the arsenic is converted into arsenious acid, and carried off in vapour, while the impure oxide of cobalt, known as *zaffre*, remains. This is dissolved in hydrochloric acid, and the remaining arsenic precipitated as sulphuret, by passing a stream of sulphuretted hydrogen through the solution. To get rid of the iron present, the last solution, after filtration, is boiled with a little nitric acid, to peroxidise that metal; carbonate of potash is added in excess, which throws down carbonate of cobalt and peroxide of iron. The precipitate is treated with oxalic acid, which forms an insoluble oxalate of cobalt and the soluble peroxalate of iron. The oxalate of cobalt is dried and decomposed by ignition in a covered crucible, when the oxide is reduced by the carbon of the acid, which goes off as carbonic acid, while the metallic cobalt remains as a black powder. To separate cobalt from nickel, with which it is almost always associated, the mixed oxalates of cobalt and nickel, obtained by the preceding process, are dissolved in ammonia, after which the liquid is diluted and exposed to the air in a shallow bason for several days. The ammonia evaporates, and the salt of nickel precipitates as a green powder, while the salt of cobalt remains in solution. The

liquid is then decanted, and if no additional precipitate subsides from it in twenty-four hours, it is free from nickel, and may be evaporated to dryness. The precipitate of nickel contains a little cobalt.

Cobalt is a brittle metal, of a reddish grey colour, somewhat more fusible than iron, and of the density 8.5131 (Berzelius.) It is generally stated to be magnetic, even when free from iron and nickel, although a minute quantity of arsenic causes it to lose that property. But Mr. Faraday finds pure cobalt not to be susceptible of magnétism. Cobalt is less oxidable in the air or by acids than iron, dissolving slowly in diluted hydrochloric or sulphuric acid, when heated, with effervescence of hydrogen; but it is readily oxidised by nitric acid. This metal forms a protoxide and peroxide, Co O and $\text{Co}_2 \text{O}_3$, corresponding with the oxides of iron, and also a compound oxide, $\text{Co O} + \text{Co}_2 \text{O}_3$, analogous to the black oxide of iron.

Protoxide of cobalt, Co O , 469 or 37.57.—Prepared by the ignition of the carbonate, this oxide is a powder of an ash grey colour. It is precipitated by an alkali, as a hydrate, from its solutions in acids, of a fine blue. Fused with glass, the oxide of cobalt colours it blue, even when in minute quantity, no other colouring matter having so much intensity. *Smalt blue* is a pounded potash glass containing cobalt. The salts of this oxide have a reddish colour in solution. They are not precipitated by sulphuretted hydrogen, when they contain a strong acid, but give a black protosulphuret with an alkaline sulphuret. The oxide is precipitated blue by ammonia, and redissolved by an excess of that alkali. It is precipitated as a pale pink carbonate by alkaline carbonates, which is soluble in carbonate of ammonia. The colour of the ammoniacal solutions of the salts of cobalt is red, which is of a lively tint when the oxide is pure, but becomes of a dull purple and even brown-black when oxide of nickel is present in greater or less quantity.

Oxide of cobalt appears to combine with alkalies and earths, as well as with acids. It dissolves in fused potash, and imparts a blue colour to the compound. Magnesia, with a drop of nitrate of cobalt, when dried and ignited, assumes a feeble but characteristic rose tint, by which the presence of that earth in minerals containing no metallic oxides nor alumina, is ascertained in blowpipe experiments. A compound of oxide of cobalt with alumina is obtained by mixing the solution of a salt

of cobalt, which must be perfectly free from iron or nickel, with a solution of equally pure alum, precipitating the liquor by an alkaline carbonate, washing the precipitate with care, drying and igniting it strongly. It forms a beautiful blue pigment, known as cobalt blue, which may be compared in purity of tint with ultramarine. A compound of oxide of cobalt with oxide of zinc may be prepared in a similar manner, which is a fine green.

Chloride of cobalt, Co Cl , is obtained by dissolving zaffre or the oxide in hydrochloric acid. Its solution is of a pink red, and affords hydrated crystals of the same colour; but when highly concentrated, the solution assumes an intense blue colour, and then affords blue crystals of chloride of cobalt, which are anhydrous, (Proust.) The red solution is used as a sympathetic ink: characters written with it on paper are colourless and invisible, or nearly so, but when the paper is warmed by holding it near a fire or against a stove, the writing becomes visible and appears of a beautiful blue. By and by, as the salt absorbs moisture, the colour again disappears, but may be reproduced by the effect of heat. If the paper be exposed to too high a temperature, the writing becomes black, and does not afterwards disappear. The addition of a salt of nickel to the sympathetic ink, gives a green instead of blue.

The neutral *carbonate of cobalt* is unknown, oxide of cobalt, like magnesia, being thrown down from its solutions, by alkaline carbonates, as a carbonate with excess of oxide. The sub-carbonate of cobalt is a pale red powder, which contains, according to Setterberger, 2 eq. of carbonic acid, 5 eq. of oxide of cobalt, and 4 eq. of water.

Besides the *sulphate of cobalt* corresponding with green vitriol, another salt was crystallized by Mitscherlich between 68° and 86° , containing 6 eq. of water, $\text{Co O}, \text{SO}_3 + 6\text{HO}$, isomorphous with a corresponding sulphate of magnesia. Sulphate of cobalt forms the usual double salts with sulphates of potash and ammonia, containing 6HO .

Phosphate of cobalt, $2\text{Co O}_2, \text{HO}, \text{PO}_5$, is an insoluble precipitate of a deep violet colour. When 2 parts of this phosphate, or 1 part of the arseniate of cobalt, is carefully mixed with 16 parts of alumina and strongly ignited for a considerable time, a beautiful blue pigment is obtained, having all the characters of ultramarine, which was discovered by Thenard.

Arseniate of cobalt, $\text{Co}_3, \text{As O}_5 + 6\text{HO}$, exists as a crystalline mineral. It contains 6HO , according to Bucholz.

Peroxide of cobalt, $\text{Co}_2 \text{O}_3$, has not the same importance as the peroxide of iron, as it does not combine with acids. It is formed when chlorine is transmitted through water in which the hydrated protoxide is suspended, or when a salt of the protoxide is precipitated by a solution of chloride of lime. In the former case, water is decomposed by the chlorine, and hydrochloric acid produced, while the oxygen of the water peroxidises the cobalt: $\text{Co}_2 \text{O}_2$ and HO and $\text{Cl} = \text{Co}_2 \text{O}_3$ and H Cl . The peroxide of cobalt is precipitated as a black hydrate, containing 2HO . This hydrate, when cautiously heated to 600° or 700° yields the black anhydrous oxide. When the peroxide of cobalt is digested in hydrochloric acid, chlorine is evolved, and the protochloride formed. Exposed to a low red heat, the peroxide loses oxygen, and the compound oxide, $\text{Co O}, \text{Co}_2 \text{O}_3$, is produced, (Hess.) When the protoxide of cobalt is calcined with a borax glass, at a moderate heat, it absorbs oxygen, and a black mass is obtained, which mixed with manganic oxide, serves as a black colour in enamel painting. A cobaltic acid, Co O_2 , was supposed to be formed by the conjoint action of oxygen and ammonia upon the protoxide, but the evidence of its existence is insufficient.

There exist three *sulphurets of cobalt*, a protosulphuret, sesquisulphuret, and bisulphuret.

Percyanide or sesquicyanide of cobalt has not been obtained in a separate state, but it exists in a class of double cyanides, of which the radical is cobalti-cyanogen, $\text{Cy}_6 \text{Co}_2$, analogous to the ferricyanides. The cobalticyanide of potassium, corresponding with the red prussiate of potash, is formed when protoxide of cobalt or its carbonate is dissolved in caustic potash, which has been treated with an excess of hydrocyanic acid. It is an anhydrous salt, pale yellow and nearly colourless when pure, of the same form as the ferricyanide of potassium. Its solution does not affect the salts of iron, but forms a rose-coloured precipitate with those of the protoxide of cobalt.

A *phosphuret of cobalt*, Co_3, P , was obtained by Rose, as a grey powder, on passing hydrogen over the subphosphate of cobalt ignited in a porcelain tube. It is also produced by the action of phosphuretted hydrogen on the chloride of cobalt, and may be looked upon as analogous in composition to the former compound, $\text{H}_3 \text{P}$.

SECTION IV.

NICKEL.

Eq. 369.7 or 29.62.

This metal resembles iron and cobalt more than any others, and is associated with these metals in meteorites, and in most of the terrestrial minerals which contain it. The principal ore of nickel is arsenical nickel, a mineral having the colour of metallic copper, to which the German miners, having attempted in vain to extract copper from it, gave the name *copper-nickel*, or false copper. This mineral was discovered, by Cronstedt of Sweden, in 1751, to contain a particular metal, which he called nickel. Nickel imparts a remarkable whiteness to the metallic alloys which contain it, on which account it has come of late to be valued in the arts, being added to brass, to form the well known imitations of silver.

The metal is prepared from the native arseniuret, or from an artificial arseniuret called *speiss*, which contains about 54 per cent of nickel, and has been observed by Wöhler in octohedrons of a square base, having the composition Ni_3As . Speiss is a metallic substance which collects at the bottom of the crucibles in which smalt or cobalt blue is prepared. In that operation, a mixture of quartz sand, potashes, and the roasted ore of cobalt are fused together. The previous roasting never being perfect, a part of the metals escape oxidation, and hence when the mixture described is fused, the cobalt, which is more oxidable than nickel and copper, reacts upon the oxides of these metals, and reduces them while it is itself oxidated: the nickel and copper concentrate in the speiss, while the smalt contains almost none of them. A salt of nickel may be obtained by treating speiss in fine powder with an equal weight of sulphuric acid, diluted with four or five times its bulk of water, and adding gradually an equal weight of nitric acid, which occasions the oxidation of both the nickel and arsenic. The green solution thus obtained, when cooled and allowed to stand for twenty-four hours, deposits much arsenious acid, from which it may be separated by filtration. A quantity of carbonate of potash, equal to half the weight of the speiss, is then added to the solution, which is

concentrated and set aside to crystallize. The double sulphate of nickel and potash, $\text{NiO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6\text{HO}$, forms easily, and may be obtained free from arsenic by a second crystallization, (Dr. Thomson.) The perfect separation of small quantities of cobalt and copper, which these crystals may still contain, requires additional processes, for which I must refer to Berzelius, (*Traité*, I, 486.) With the view of obtaining the metal, the insoluble oxalate of nickel may be precipitated from the preceding salt by oxalate of ammonia, washed, dried, and ignited gently in a covered crucible. The oxalic acid reduces the oxide of nickel, and the metal remains in a spongy state. It is pyrophoric, like manganese and iron prepared in the same manner, if the temperature of reduction has been low. To obtain the metal in a solid mass, it should be fused in a crucible covered with pounded glass. The oxide of nickel is very easily reduced both by carbonic oxide and hydrogen.

Nickel, when free from cobalt, is silver white, unalterable in air, and highly ductile. Its density, according to Richter, is 8.279, and after being forged, 8.666. Nickel is magnetic nearly to the same extent as iron. Magnets composed of this metal lose their polarity at 630° (Faraday.) It is somewhat more fusible than iron. Nickel forms two oxides corresponding with the protoxide and peroxide of iron; but the double compound of the two oxides of nickel, corresponding with the black oxide of iron, has not been observed.

Protoxide of nickel, NiO ; 469.7 or 37.62.—May be obtained by the ignition of the carbonate or nitrate of nickel, or by precipitation from its salts by an alkali, as a dark ash-coloured powder, or as a bulky hydrate, of an apple-green colour, NiO, HO . Oxide of nickel is very soluble in acids, but not in potash or soda. Ammonia dissolves it, and forms an azure blue solution, from which oxide of nickel is precipitated by potash, barytes, and strontian, having a considerable tendency to combine with salifiable bases. The solutions of its salts have all a green colour, much more intense than that of the ferrous salts. They are not precipitated by sulphuretted hydrogen when a strong acid is present, but afford a black sulphuret with alkaline sulphurets. The carbonate of nickel is of a pale green colour, and soluble in carbonate of ammonia.

Peroxide of nickel, Ni_2O_3 , is obtained as a black powder, by exposing the hydrated protoxide suspended in water to a

stream of chlorine gas. It does not combine with acids, and in other respects resembles peroxide of cobalt.

Besides a *protosulphuret*, NiS , a *subsulphuret of nickel*, Ni_2S , is formed, like that of manganese, by decomposing the ignited sulphate of nickel by hydrogen. A *bisulphuret of nickel* also exists in combination as a constituent of the mineral, nickel-glance, $\text{NiS}_2 + \text{NiAs}$.

Chloride of nickel, NiCl , forms a solution of an emerald green colour, and yields by evaporation a hydrated salt of the same colour, which becomes yellow when deprived of its water of crystallization. Chloride of nickel, sublimed at a high temperature without access of air, forms golden scales, which dissolve with difficulty.

Sulphate of nickel crystallizes from a strong solution in slender green prisms, isomorphous with epsom salt, of which the composition is $\text{NiO}, \text{SO}_3 + 7\text{HO}$. At a higher temperature, it crystallizes with 6 eq. of water, $\text{NiO}, \text{SO}_3 + 6\text{HO}$, like the magnesia and cobalt salt, and in the same form. M. Mitscherlich has made the singular observation, that when the crystals containing 7 eq. of water are exposed, in a close glass vessel, to a day of sunshine, or kept for some time in a temperate place, they change their form, becoming a mass of small crystals, of which the form is the regular octohedron. The original crystals become opaque from this change, but lose none of their combined water. Sulphate of nickel forms the usual double salts with sulphates of potash and ammonia.

The useful white *alloy of nickel*, German silver, or *packfong*, is formed by fusing together 100 parts of copper, 60 of zinc, and 40 of nickel.

SECTION V.

ZINC.

Eq. 403.2 or 32.31; Zn.

The principal ores of zinc are *calamine*, or the carbonate, a pulverulent mineral generally of a reddish or flesh colour, and *zinc blende*, a massive mineral of an adamantine lustre, and often black. The oxide, from the carbonate or from the calcined sulphuret, is reduced by means of carbonaceous matter. This process is conducted in a distillatory apparatus, of a particular

form, owing to the volatility of the metal. It consists of a crucible, covered above, with an iron tube in its bottom, of which the upper open extremity is in the crucible, and the other terminates over a vessel of water below the furnace. The gaseous products and vapour of zinc escape by this tube, and the latter is condensed in the water. Zinc may be purified by a second distillation in a porcelain retort, but the first portions of that metal which come over should be rejected, as they generally contain cadmium and arsenic.

Zinc is a white metal, with a shade of blue, and possessing a bright metallic lustre. It is usually brittle, and its fracture exhibits a crystalline structure. But zinc, if pure, may be hammered into thin leaves, at the usual temperature; and commercial zinc, which is impure and brittle at a low temperature, acquires the same malleability between 210° and 300° : it may then be laminated; and the metal is now consumed in the form of sheet zinc for a variety of useful purposes. At 400° it again becomes brittle, and may be reduced to powder in a mortar of that temperature. The density of cast zinc is 6.862, but it may be increased by forging to 7.21. Its point of fusion is 773° , (Daniell.) At a red heat, zinc rises in vapour, and takes fire in air, burning with a white flame like that of phosphorus; the white oxide produced is carried up mechanically in the air, although itself a fixed substance. Laminated zinc is a valuable substance, from its little disposition to undergo oxidation. When exposed to air, or placed in water, its surface becomes covered with a grey film of suboxide, which does not increase; this film is better calculated to resist both the mechanical and chemical effects of other bodies than the metal itself, and preserves it. Zinc dissolves with facility in dilute hydrochloric, sulphuric and other hydrated acids, by substitution for hydrogen. In contact with iron, it protects the latter from oxidation in any saline fluid. Zinc forms probably three oxides, the suboxide referred to, the protoxide, and a peroxide, when the hydrated protoxide is acted upon by a solution of peroxide of hydrogen; but of these, the first and last have not been studied, and the protoxide is, therefore, the only well known oxide of zinc.

Protoxide of zinc; ZnO ; 503.2 or 40.31.—May be obtained by the combustion of the metal in a stoneware crucible, as a white powder, or by precipitation from its salts, by an alkali, as a white hydrate. It is of a yellow colour at a high tempera-

ture, which disappears on cooling. Oxide of zinc combines with acids and forms salts, which are colourless like those of magnesia. It is precipitated as a white gelatinous hydrate, by ammonia, and redissolved by an excess of that alkali. It is soluble also in potash and soda, and combines with several other basic oxides. Its salts, containing a strong acid in excess, are not affected by sulphuretted hydrogen, but give a white hydrated sulphuret with an alkaline sulphuret. By the oxidation of zinc in air and water, without access of carbonic acid, a hydrate, $3\text{Zn O} + \text{HO}$, has been obtained in crystalline needles, (Mitscherlich.)

The native *sulphuret of zinc*, or zinc blende, Zn S ; crystallizes in octohedrons. Its colour is variable, being sometimes yellow, red, brown or black.

Chloride of zinc, Zn Cl , is produced by the combustion of zinc in chlorine, and by dissolving the metal in hydrochloric acid. It is fusible at 212° , volatile at a red heat, and perhaps the most deliquescent of salts.

Iodide of zinc, is formed by digesting iodine, zinc and water together, and resembles the chloride.

The neutral *carbonate of zinc*, forms the ore of zinc, calamine. When precipitated by an alkaline carbonate, the salts of zinc, like those of magnesia, yield the neutral carbonate in combination with hydrated oxide, $2(\text{Zn O}, \text{CO}_2) + 3(\text{Zn O}, \text{HO})$. The mineral substance, *zinc bloom*, is of the same composition. Precipitated in the cold, the carbonate is $\text{ZnO}, \text{CO}_2 + 2(\text{ZnO}, \text{HO})$, but is contaminated by sulphate of soda, (Mitscherlich.)

Sulphate of zinc, *White vitriol*, $\text{ZnO}, \text{SO}_3 + 7\text{HO}$.—This salt is formed by the oxidation of the native sulphuret at a high temperature, or by dissolving the metal in dilute sulphuric acid. It crystallizes in colourless prismatic crystals, containing 7 eq. of water, of which the form is a right rhombic prism. These crystals are soluble in $2\frac{1}{2}$ times their weight of water, at the usual temperature, and fuse in their water of crystallization, when heated. It also crystallizes above 86° , with 6 eq. of water, in an oblique rhombic prism (Mitscherlich). Another hydrate is formed and precipitated as a white powder, according to Kuhn, containing 2 eq. of water, when a concentrated solution of sulphate of zinc is mixed with oil of vitriol. The sulphate of zinc forms the usual double salt with sulphate of potash, $\text{ZnO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6\text{HO}$. The double sulphate of

zinc and soda contains 4 atoms of water, $\text{ZnO}, \text{SO}_3 + \text{NaO}, \text{SO}_3 + 4\text{HO}$. It is formed by a singular decomposition (page 190). When a solution of the sulphate is mixed with a quantity of alkali less than sufficient for complete precipitation, a *subsulphate of zinc* precipitates, which according to the analyses of several chemists, contains 4 eq. of oxide of zinc to 1 eq. of sulphuric acid, besides water. A concentrated solution of sulphate of zinc dissolves the preceding subsalt, and when saturated contains a compound of 1 eq. of acid and 2 eq. of base, according to Schindler, and does not crystallize. From this solution Schindler obtained the former insoluble subsalt with two different proportions of water, in long crystalline needles, containing 10HO , by the spontaneous evaporation of the solution, and in brilliant crystalline plates, containing 2HO , which were deposited on boiling the solution. He also obtained another subsalt, by diluting the same solution with a large quantity of water, as a light bulky precipitate, which contained 1 eq. of acid, 8 eq. of oxide of zinc, and 2 eq. of water. The insoluble matter which precipitates when dry sulphate of zinc combined with 1 eq. of ammonia (page 412), is thrown into water, is considered, by Dr. Kane, a third subsulphate of zinc, containing 1 eq. of acid, 6 eq. of oxide of zinc, and 10 eq. of water. All these subsulphates afford neutral sulphate of zinc to water, after being heated to redness, so that whatever their constitution may be, when hydrated, it is certainly different from what it is in their anhydrous condition.

Nitrate of zinc, $\text{ZnO}, \text{NO}_5 + 6\text{HO}$, is very soluble in water, and moderately deliquescent.

Phosphate of zinc, $\text{ZnO}_2. \text{HO}, \text{PO}_5 + 2\text{HO}$, is obtained in minute silvery plates, which are nearly insoluble, on mixing dilute solutions of phosphate of soda and sulphate of zinc.

Silicate of zinc is found as a crystalline mineral, which has received the name of the electrical oxide of zinc, because it acquires, like the tourmalin, a high degree of electrical polarity when heated. It contains water, and may be represented by the formula $2(3\text{ZnO}, \text{SiO}_3) + 3\text{HO}$.

The most important *alloys of zinc* are those with copper, which form the varieties of brass. Zinc also combines readily with iron, and is contaminated by that metal, when fused in an iron crucible.

SECTION VI.

CADMIUM.

Eq. 696.8 or 55.83; Cd.

This metal is frequently found in small quantity with zinc, and derives the name cadmium, applied to it by Stromeyer, from *cadmia fossilis*, a denomination by which the common ore of zinc was formerly designated. In the process of reducing ores of zinc, the cadmium which they contain comes over among the first products of distillation, owing to the great volatility of that metal. It may be separated from zinc, in an acid solution, by sulphuretted hydrogen, which throws down cadmium as a yellow sulphuret. This sulphuret dissolves in concentrated hydrochloric acid, affording the chloride of cadmium, from which the carbonate may be precipitated by an excess of carbonate of ammonia. Carbonate of cadmium is converted by ignition into the oxide, and the latter yields the metal when mixed with one-tenth of its weight of pounded coal, and distilled in a glass or porcelain retort, at a low red heat.

Cadmium is a white metal, like tin, very ductile and malleable. It fuses considerably under a red heat, and is nearly as volatile as mercury. The density of cadmium, cast in a mould, is 8.604, after being hammered, 8.6944. Cadmium may be dissolved in the more powerful acids, by substitution for hydrogen, with the aid of heat; but nitric acid is its proper solvent.

Oxide of cadmium, CdO ; 796.8 or 63.83.—The only known oxide of cadmium is obtained by the combustion of the metal, or by the ignition of its carbonate, as a powder of an orange colour, or as a white hydrate by precipitation from its salts by an alkali. Its density, in the anhydrous condition, is 8.183, (Herapath.) This oxide is soluble in ammonia, but not in its carbonate, (differing in the last property from zinc and copper), nor in the fixed alkalies. Its salts are white, and greatly resemble those of zinc. They are precipitated of a fine yellow by sulphuretted hydrogen.

Sulphuret of cadmium is distinguished from sulphuret of arsenic, which it resembles in colour, by being insoluble in potash, and by sustaining a red heat without subliming.

Chloride and iodide of cadmium are easily crystallized in combination with water.

Sulphate of cadmium forms efflorescent crystals, $\text{CdO}, \text{SO}_3 + 4\text{HO}$; and forms a double salt with sulphate of potash: $\text{CdO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6\text{HO}$.

Several definite *alloys of cadmium* have been formed. At a red heat, 100 parts of platinum retain 117.3 parts of cadmium, giving a compound Cd_2Pt : 100 parts of copper retain, at a red heat, 82.2 of cadmium, which approaches nearly the proportion of CdCu_2 . Cadmium forms an amalgam with mercury, which crystallizes in octohedrons, and consists of 21.74 parts of cadmium, and 78.26 of mercury, or Cd Hg_2 .

SECTION VII.

COPPER.

Eq. 395.7 or 31.71; Cu (cuprum.)

Copper, if not the most abundant, is certainly one of the most generally diffused of the metals. Its ores are often accompanied by metallic copper, crystallized in cubes or octohedrons. The richest mines of this country are those in Cornwall and Anglesea. The common ore of this metal is *copper pyrites*, a compound of subsulphuret of copper and sesquisulphuret of iron, or a sulphur salt, $\text{Cu}_2\text{S} + \text{Fe}_2\text{S}_3$, but in which the two sulphurets are also found in other proportions, and which often contains an admixture of the bisulphuret of iron. Few metallurgic processes require more skill and attention than the extraction of copper from this ore. The first object of the process is, by roasting the ore at a high temperature, in contact with siliceous matter, to oxidate and convert the iron into a fusible silicate or slag, while the less oxidable copper is obtained as the fusible subsulphuret of copper, but still contaminated with a considerable quantity of protosulphuret of iron. By alternate oxidation of the last product, and reduction by carbonaceous matter in contact with quartz sand, more of the iron and other oxidable substances are separated in the form of scoriæ, and the same end is afterwards more perfectly attained by directing a strong blast of air upon the surface of the melted copper.

With the exception of titanium, copper is the only metal of a red colour. The crystals of native copper, and of that obtained in the humid way by precipitation with iron, belong to the regular system; but the crystals which form in the cooling of melted copper were found by Seebeck to be rhomboidal, and to have a different place in the thermo-electric series from the other crystals. The density of copper when cast is about 8.83, and when laminated or forged 8.95 (Berzelius.) It is less fusible than silver, but more so than gold, its point of fusion being 1996° (Daniell.) It is one of the most highly malleable metals, and in tenacity is only inferior to iron. It has much less affinity for oxygen than iron, and decomposes water only at a bright red heat, and to a small extent. In damp air, it acquires a green coating of subcarbonate of copper, and its oxidation is remarkably promoted by the presence of acids. The weaker acids, such as acetic, have no effect upon copper, unless with the concurrence of the oxygen of the air, when the copper rapidly combines with that oxygen, and a salt of the acid is formed. Copper scarcely decomposes the hydrated acids, by displacing hydrogen; for when boiled in hydrochloric acid, it disengages only the smallest traces of that gas. But hydrogen does not precipitate metallic copper from solution. Copper acts violently on nitric acid, occasioning its decomposition, with evolution of nitric oxide, and dissolving as a nitrate.

Suboxide of copper, Red oxide of copper, Cu_2O ; 891.4 or 71.42.—This degree of oxidation is better marked in copper than in any other metal of the magnesian class. The suboxide of copper is found native in octohedral crystals, and may be prepared artificially by heating to redness, in a covered crucible, a mixture of five parts of the black oxide of copper with four parts of copper filings. It is a reddish brown powder, which undergoes no change in the air. The surface of vessels of polished copper is often converted into suboxide, or bronzed, to enable them to resist the action of air and moisture: this is done by covering them with a paste of peroxide of iron, heating to a certain point, and afterwards cleaning them, to remove the oxide of iron; or otherwise, by means of a boiling solution of acetate of copper.

Dilute acids decompose suboxide of copper, dissolving the protoxide, and leaving metallic copper. Undiluted hydrochloric acid dissolves the suboxide, without decomposition, or rather

forms a corresponding subchloride of copper, which is soluble in hydrochloric acid. The hydrated alkalies precipitate a hydrated suboxide from that solution, of a lively yellow colour, which changes rapidly in air from absorption of oxygen.

Suboxide of copper is also formed when copper is placed in a dilute solution of ammonia, containing air, and is dissolved by the alkali. If the ammonia has been corked up in a bottle with copper for some time, the liquid is colourless; but on pouring it out in a thin stream, it immediately becomes blue, by absorbing oxygen. The liquid may be again deprived of colour by returning it to the bottle, and closing it up, in contact with the metal.

Compounds have been obtained of suboxide of copper with several acids, particularly with sulphurous acid, the sulphite forming a double salt with sulphite of potash, $\text{Cu}_2\text{O}, \text{SO}_2 + 2(\text{KO}, \text{SO}_2)$, with hyposulphurous acid, with sulphuric, carbonic and acetic acids. When fused with vitreous matter, the suboxide of copper gives a beautiful ruby red glass; but it is difficult to prevent the suboxide from absorbing oxygen, when the glass becomes green.

Subsulphuret of copper, Cu_2S , forms the mineral *copper glance*, and is also a constituent of copper pyrites. It is a powerful sulphur base. Copper filings, mixed with half their weight of sulphur, when heated, unite with intense ignition, and form this subsulphuret.

Subchloride of copper, Cu_2Cl , may be prepared by heating copper filings with twice their weight of corrosive sublimate. It was obtained by Mitscherlich in tetrahedrons, by dissolving in hydrochloric acid the subchloride of copper formed on mixing solutions of protochlorides of copper and tin, and allowing the concentrated solution to cool. Subchloride of copper so prepared is white, insoluble in water, soluble in hydrochloric acid, but precipitated by dilution. It is dissolved by a boiling solution of chloride of potassium, which, if allowed to cool in a close vessel, yields large octohedral crystals of a double chloride: $\text{Cu}_2\text{Cl} + 2\text{KCl}$; they are anhydrous. It is remarkable that the forms of this double salt, and of both its constituents, all belong to the regular system.*

Subiodide of copper, Cu_2I , is a white insoluble precipitate,

* Mitscherlich in Poggendorff's Annalen, 49, 401. 1840.

obtained on mixing a solution of 1 part of sulphate of copper and $2\frac{1}{4}$ parts of protosulphate of iron, with a solution of iodide of potassium.

Protoxide of copper, Black oxide of copper, CuO ; 495.7 or 39.71.—The base of the ordinary salts of copper. It is formed by the oxidation of copper at a red heat, but is generally prepared by igniting the nitrate of copper. It is black like charcoal, and fuses at a high temperature. This oxide is remarkable for the facility with which it is reduced, at a low red heat, by hydrogen and carbon, which it converts into water and carbonic acid. It is that property which recommends oxide of copper for the combustion of organic substances, in close vessels, by which their ultimate analysis is effected. The protoxide of copper precipitates as a blue hydrate, when a solution of sulphate of copper is allowed to fall, drop by drop, into solution of potash. This hydrate is decomposed in boiling water, and becomes brown, but is apt to carry down a little of its precipitating alkali, of which it is difficult to deprive the brown oxide altogether by washing.

The oxide of copper dissolves readily in ammonia, affording a deep azure blue solution. But for this experiment a small quantity of acid, or of a salt of ammonia, must be present, the solution appearing to be truly that of a subsalt of copper in ammonia, and pure ammonia not dissolving equally pure oxide of copper. Dr. Kane obtained, on one occasion, an insoluble *ammoniacal oxide of copper*, by precipitating chloride of copper by ammonia, of which the composition was $3\text{CuO} + 2\text{NH}_3 + 6\text{HO}$.

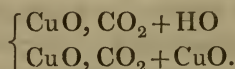
Oxide of copper is a powerful base. Its salts are generally blue or green, when hydrated, but white when anhydrous. Although neutral in composition, they have a strong acid reaction. They are poisonous; but their effect upon the animal system is counteracted in some degree by sugar. Liquid albumen forms insoluble compounds with these salts, and is an antidote to their poisonous action. Copper is separated in the metallic state from its salts by zinc, iron, lead, and the more oxidable metals, which are dissolved and take the place of the former metal. Copper is completely precipitated by sulphuretted hydrogen, as a dark brown or black sulphuret, even from acid solutions. The ferrocyanide of potassium gives a characteristic brown precipitate with the salts of copper. Its salts also impart a green colour to flame. The black oxide of copper

dissolves by fusion in a vitreous flux, and produces a green glass.

Thenard obtained a higher oxide of copper, CuO_2 , by the action of diluted peroxide of hydrogen on the hydrated protoxide.

Chloride of copper, $\text{CuCl} + 2\text{HO}$, is obtained by dissolving the black oxide in hydrochloric acid. Its solution, when concentrated is green, but the salt forms blue prismatic crystals, which contain two atoms of water. It combines with chloride of potassium, and more readily with chloride of ammonium, forming the double salts, $\text{KCl} + \text{CuCl} + 2\text{HO}$, and $\text{NH}_4\text{Cl} + \text{CuCl} + 2\text{HO}$.

Carbonates of copper.—When a salt of copper is precipitated by an alkaline carbonate, a hydrated subcarbonate is produced, containing 2 eq. of oxide of copper to 1 eq. carbonic acid. It is a pale blue bulky precipitate, which becomes denser and green when treated with boiling water. It is used as a pigment, and known as *mineral green*. The beautiful native green carbonate of copper, *malachite*, is of the same composition, $\text{CuO}, \text{CO}_2 + \text{CuO}, \text{HO}$. The finely crystallized *blue copper ore* is another subcarbonate. It may be represented as the neutral hydrated carbonate of copper, in combination with a similar carbonate of copper, in which the constitutional water is replaced by oxide of copper :



In the green carbonate, the constitutional water of the neutral carbonate of copper is replaced by hydrate of copper. The neutral carbonate of copper itself, of which the formula would be $\text{CuO}, \text{CO}_2 + \text{HO}$, is unknown.

Sulphate of copper, *Blue vitriol*, $\text{CuO}, \text{SO}_3, \text{HO} + 4\text{HO}$; 996.9 + 562.5 or 79.88 + 45.—This salt may be formed by dissolving copper in sulphuric acid diluted with half its bulk of water with ebullition, when the metal is oxidated with formation of sulphurous acid. But the sulphate of copper is more generally prepared, on the large scale, by the roasting and oxidation of sulphuret of copper. It forms large rhomboidal crystals of a sapphire blue, containing 5 eq. of water, which lose their transparency in dry air : they are soluble in four times their weight of cold, and twice their weight of boiling water. Like

the other soluble salts of copper, the sulphate has an acid reaction; it is used as an escharotic. The water in this salt may be reduced to 1 eq. at 212° ; above 400° it is anhydrous and white. Although pure sulphate of copper does not crystallize with 7HO , yet, when mixed with sulphates of magnesia, zinc, nickel, and iron, it crystallizes along with these isomorphous salts in the form of sulphate of iron. At a strong red heat, it fuses and loses acid. The anhydrous sulphate absorbs $2\frac{1}{2}$ eq. of ammonia, and forms a light powder of a deep blue colour. When ammonia is added to a solution of sulphate of copper, an insoluble subsulphate is first thrown down, which is redissolved as the addition of ammonia is continued, and the usual deep azure blue ammoniacal solution formed. The ammoniacal sulphate may be obtained in beautiful indigo-blue crystals, by conducting a stream of ammoniacal gas into a saturated hot solution of the sulphate: it is $\text{CuO}, \text{SO}_3, \text{HO} + 2\text{NH}_3$ (Berzelius.) These crystals lose 1 eq. ammonia and 1 eq. water at 390° (Kane), and are converted into a green powder, $\text{CuO}, \text{SO}_3 + \text{NH}_3$, or $(\text{NH}_3\text{CuO})\text{SO}_3$ (page 415); by the cautious application of a heat not exceeding 500° , the whole ammonia may be got rid of, and sulphate of copper quite pure remains behind. Sulphate of copper forms the usual double salts with sulphate of potash and with sulphate of ammonia. A saturated hot solution of the double sulphate of copper and potash allows a remarkable double subsalt to precipitate in crystalline grains, $\text{KO}, \text{SO}_3 + 3(\text{CuO}, \text{SO}_3) + \text{CuO}, \text{HO} + 3\text{HO}$. A corresponding seleniate falls, under the boiling point, and always in crystals. The ammoniacal and double salts of sulphate of copper may be represented thus:

Sulphate of copper (blue vitriol) . . .	$\text{CuO}, \text{SO}_3, \text{HO} + 4\text{HO}$
Sulphate of copper and potash . . .	$\text{CuO}, \text{SO}_3, (\text{KO}, \text{SO}_3) + 6\text{HO}$
Hydrated ammoniacal sulphate of copper . . .	$\text{CuO}, \text{SO}_3, \text{HO} + 2\text{NH}_3$
Preceding salt dried at 300° . . .	$(\text{NH}_3\text{CuO}), \text{SO}_3$
Rose's ammoniacal sulphate . . .	$\text{CuO}, \text{SO}_3 + (\text{NH}_3\text{CuO})\text{SO}_3 + 4\text{NH}_3$
Do. heated to 350° . . .	$\text{CuO}, \text{SO}_3 + (\text{NH}_3\text{CuO})\text{SO}_3$

Several *subsulphates of copper* have been formed. A green powder is obtained by digesting hydrated oxide of copper in a solution of sulphate of copper, of which the constituents are, according to Berzelius, $\text{SO}_3, 3\text{CuO}$ and 3HO . The bluish green precipitate which falls when ammonia is added to sulphate of

copper, or potash added in moderate quantity to the same salt, contains, according to Kane's analysis and my own, $\text{SO}_3, 4\text{CuO}$ and 4HO . By a larger quantity of potash, Dr. Kane precipitated a clear grass green subsulphate, containing $\text{SO}_3, 8\text{CuO}$ and 12HO . The last subsulphate loses exactly half its water at 300° .*

Nitrate of copper, $\text{CuO}, \text{NO}_5 + 3\text{HO}$, is formed by dissolving copper in nitric acid. It crystallizes from a strong solution in blue prisms, which contain 3 atoms of water, or in rhomboidal plates, which contain 6 atoms of water. This salt acts upon granulated tin, with nearly as much energy, as hydrated nitric acid. A crystallized *ammoniacal nitrate of copper*, is obtained by conducting a stream of ammoniacal gas into a saturated solution of nitrate of copper. It is anhydrous, and contains NO_5, CuO and 2NH_3 (Kane). I would prefer to represent it as a nitrate of cuprammonium + 1 eq. of ammonia, that is, $(\text{NH}_3, \text{CuO}) \text{NO}_5 + \text{NH}_3$.

Subnitrate of copper, $\text{HO}, \text{NO}_5 + 3\text{CuO}$, is a green powder, produced by the effect of heat upon the neutral nitrate, at any temperature between 150° and 600° ; or by adding a quantity of alkali to that salt, insufficient for complete precipitation. When oxide of copper is drenched with the most concentrated nitric acid (HO, NO_5), it is this subsalt, singular as it may appear, which is formed, even when the acid is in great excess; the reason seems to be, that the nitrate of water, being deficient in constitutional water, assumes 3 atoms of oxide of copper in its place (page 296).

Oxalate of copper and potash, is obtained by dissolving oxide of copper in binoxalate of potash; it crystallizes with both 2 and 4 atoms of water.

Acetates of copper.—The *neutral acetate*, $\text{CuO}, (\text{C}_4\text{H}_3\text{O}_3) + \text{HO}$, is obtained by dissolving oxide of copper in acetic acid. It forms fine crystals of a deep green colour, containing 1 eq. of water, which lose their transparency in air, and are soluble in 5 times their weight of boiling water. This salt also forms blue crystals from an acid solution, under 40° , which contain 5HO (Wöhler). The green salt is found in commerce under the improper name of *distilled verdigris*. Acetates of copper and potash unite in single equivalents, and form a double salt

* Transactions of the Royal Irish Academy, vol. 19, p. 1; or An. de Ch. et de Ph. t. 72, p. 272.

in fine blue crystals, containing 8HO. *Verdigris* is a subacetate of copper, formed by placing plates of the metal in contact with the fermenting marc of the grape, or with cloth dipt in vinegar. The bluer species, which consists of minute crystalline plates, is a definite compound of 1 eq. acetic acid, 2 eq. oxide of copper, and 6 eq. of water, $\text{CuO}, (\text{C}_4 \text{H}_3 \text{O}_3), \text{CuO} + 6\text{HO}$. The ordinary green species is a mixture of sesqui and tribasic acetates of copper, with the preceding bibasic acetate. Water dissolves out from verdigris the *sesquiacetate*, which presents itself on evaporating the solution, sometimes as an amorphous mass, and sometimes in crystalline grains of a pale blue colour. It consists of 2 eq. of acetic acid, 3 eq. of oxide of copper and 6 eq. of water; it loses 3 eq. of water at 212° . The *tribasic acetate* is the insoluble residue which remains, after the lixiviation of verdigris. It is a clear green powder, which loses nothing at 212° . It contains 2 eq. of acetic acid, 6 eq. oxide of copper, and 3 eq. of water. (Berzelius).

Acetate of copper also combines with acetate of lime, and with several other salts. The double *acetate and arsenite of copper*, is a crystalline powder of a brilliant sea-green colour, which is used as a pigment, under the name of the green of Schweinfurth. It is obtained by mixing boiling solutions of equal parts of arsenious acid, and the neutral acetate of copper, adding to the mixture its own volume of cold water, and leaving the whole at rest for several days. It is a highly poisonous substance. From the analysis of Ehrmann its formula is $\text{Cu O}, (\text{C}_4 \text{H}_3 \text{O}_3) + 3(\text{Cu O}, \text{As O}_3)$.

The most important *alloys of copper* are those with tin and zinc:

100 parts copper with 10 tin, form bronze and gun metal.

100 parts copper with 20 to 25 tin, form bell metal.

100 parts copper with 30 to 35 tin, form speculum metal.

A little arsenic is generally added to the last alloy, to increase its whiteness.

The different varieties of brass are prepared, either by fusing together the two metals, copper and zinc, or by heating copper under a mixture of charcoal and calamine, an operation in which zinc is reduced and its vapour absorbed by the copper. Two or three parts of copper to one of zinc form common brass; equal parts of copper and zinc, or four of the former and one of the latter, give an alloy of a higher colour resembling gold, and on that account called *similor*.

SECTION VIII.

LEAD.

Eq. 1294.5 or 103.73 ; Pb (plumbum).

Lead was one of the earliest known of the metals. A considerable number of its compounds are found in nature, but the sulphuret, or galena, is the only one which is important as an ore of lead. The reduction of the metal is effected by heating with exposure to air (or roasting) the sulphuret, by which much of the sulphur is burned and escapes as sulphurous acid, and a fusible mixture of oxide of lead and sulphate of lead is produced. A fresh portion of the ore is added, which reacts upon the oxide of lead, the sulphur and oxygen forming sulphurous acid, and the lead of both oxide and sulphuret being consequently reduced. Lime also is added, which decomposes the sulphate of lead, and exposes the oxide to be reduced by the fuel or by sulphuret.

Lead has a bluish grey colour and strong metallic lustre, is very malleable, and so soft, when it has not been cooled rapidly, as to produce a metallic streak upon paper. Its density is 11.445, and is not increased by hammering. Its tenacity is less than that of any other ductile metal. The melting point of lead is 612° ; on solidifying, this metal shrinks considerably, so that bullets cast in a mould are never quite round. Lead, like most other metals, assumes the octohedral form on crystallizing. Lead is one of the less oxidable metals, at least, when massive; its surface soon tarnishes, and is covered with a grey pellicle, which appears to defend the metal from farther change. Rain or soft water cannot be preserved with safety in leaden cisterns, owing to the rapid formation of a white hydrated oxide at that line where the metal is exposed to both air and water; the oxide formed is soluble in pure water, and highly poisonous. But a minute trace of any sulphate or chloride in the water, which spring and well water usually contain, arrests the corrosion of the lead, by converting the oxide of lead into an insoluble salt, and prevents the contamination of the water, (Dr. Christison's Treatise on Poisons). Lead is not directly attacked by hydrochloric and sulphuric acids, at the usual tem-

perature, but they favour its union with oxygen from the air. Its best solvent is nitric acid. Besides a protoxide, PbO , which is a powerful base, lead forms a suboxide Pb_2O , and a peroxide PbO_2 , which do not combine with acids.

Suboxide of lead, Pb_2O , was discovered by Dulong, and is best obtained by heating the oxalate of lead to low redness in a small retort. It is dark grey, almost black, and pulverulent, and is not affected by metallic mercury. By the analysis of Boussingault, it contains 1 eq. of oxygen to 2 eq. of lead. The grey pellicle which forms upon lead exposed to the air is, according to Berzelius, the same suboxide.

Protoxide of lead, PbO , 1394.5 or 111.73.—When a stream of air is thrown upon the surface of melted lead, the metal is rapidly converted into the protoxide, of a sulphur-yellow colour. The oxidated skimmings of the metal are, in this condition, termed *massicot*, and were at one time used as a yellow pigment. This preparation is fused at a bright red heat, and the oxide is thus separated from some metallic lead, with which it is intermixt in *massicot*. The fused oxide forms a brick red mass, on solidifying, which divides easily into crystalline scales, which are tough and not easily pulverised; they form *litharge*. The protoxide of lead can be obtained distinctly crystallized by various processes, but always presents itself in the same form, an octohedron with a rhombic base (Mitscherlich). By igniting the subnitrate of lead, the protoxide is obtained very pure, and of a rich lemon yellow colour. Its density when fused is 9.4214.

When the acetate, or any other salt of lead, is precipitated by potash, the protoxide falls as a white hydrate, which may be dried at 212° without decomposition. It contains $3\frac{3}{4}$ per cent water, and is, therefore, the hydrate $2\text{PbO} + \text{HO}$, (Mitscherlich). Oxide of lead likewise crystallizes anhydrous, from solution, at the usual temperature, when water to combine with is denied to it, in the circumstances of its precipitation. This oxide dissolves in above 12,000 times its weight of distilled water, which acquires thereby an alkaline reaction; but not in water containing any saline matter. It is soluble in potash or soda; and the solutions, when evaporated, afford small crystals of an alkaline compound. A compound of lime and oxide of lead is obtained in needles, when hydrate of lime and that oxide are heated together, and the solution allowed to evaporate with exclusion of air. This

solution has been employed to dye the hair black. The oxide of lead combines readily with the earths and metallic oxides by fusion, and when added to the materials of glass imparts brilliancy to it and increased fusibility.

Oxide of lead is a powerful base, resembling barytes and strontian, and affords a class of salts which often agree in form and in general properties with the salts of these earths. Its carbonate occurs in *plumbocalcite*, in the form of carbonate of lime; an isomorphism by which the protoxide of lead is connected with the magnesian oxides. All its soluble salts are poisonous, although no salt of lead, with the exception of the carbonate, which is insoluble, is highly so (Dr. A. T. Thomson). Lead is precipitated by sulphuretted hydrogen, as a black sulphuret, even from acid solutions. Neutral salts of lead are also precipitated by solutions of carbonates, chlorides, sulphates, phosphates, etc., the corresponding salts of lead being insoluble. Iodide of potassium and red chromate of potash produce yellow precipitates in salts of lead, which are highly characteristic of the metal. Iron and zinc throw down metallic lead. If a mass of zinc be suspended in a solution, made by dissolving one ounce of acetate of lead in two pounds of distilled water, the lead is precipitated in beautiful crystalline plates, which are deposited only in metallic contact with the zinc, but extend from it to a considerable distance in the liquid, forming what is called the lead tree.

Peroxide of lead, PbO_2 , may be obtained in the same manner as the peroxides of cobalt and nickel, exposing the protoxide suspended in water to a stream of chlorine; also by fusing protoxide of lead with chlorate of potash at a temperature short of redness; or by digesting the following intermediate oxide, minium, in diluted nitric acid, which dissolves protoxide of lead, decanting off the nitrate of lead, and washing the powder which remains with boiling water. Peroxide of lead is of a dark earthy brown colour. It loses half its oxygen by ignition, absorbs sulphurous acid with great avidity and becomes sulphate of lead, affords chlorine when digested in hydrochloric acid, and the nitrate of protoxide of lead with water, when digested in ammonia.

Minium or Red lead is formed by heating massicot or protoxide of lead, which has not been fused, to incipient redness in a flat furnace, of a particular construction, and directing a cur-

rent of air upon its surface. Oxygen is absorbed, and an oxide formed of a fine red colour, with a shade of yellow. It is not constant in composition. The proportion of oxygen, when the absorption is least considerable, approaches that of a compound $3\text{PbO} + \text{PbO}_2$, and such was the composition of a crystallized compound of a fine red colour, formed by accident in a minium furnace, and analyzed by Houton-Labillardière. But when the absorption is favoured by time and most considerable, it approaches, but never exceeds 2.4 per cent of the original weight of the protoxide, which gives a compound of $2\text{PbO} + \text{PbO}_2$, according to the observations of M. Dumas. The proportion of 3 eq. of metal to 4 eq. of oxygen, which minium thus possesses, is a very common one, but generally due to the combination of a protoxide with a peroxide, the latter containing 2 atoms of metal and 3 atoms of oxygen, as the peroxide of iron. Berzelius considers the composition of minium to favour the existence of such an oxide of lead Pb_2O_3 ; minium would then be represented as $\text{PbO} + \text{Pb}_2\text{O}_3$. The finest minium is obtained by calcining oxide of lead from the carbonate, at about 600° .

Minium is not altered by being heated in a solution of acetate of lead, which is capable of dissolving free protoxide of lead. When heated to redness it loses oxygen, and the protoxide remains. It does not combine with acids, but is resolved by a strong acid into peroxide of lead, and protoxide, the last combining with the acid. When minium is treated with concentrated acetic acid, it first becomes white, then dissolves entirely in a new quantity of acid without colouring it. But the solution gradually decomposes, and peroxide of lead separates from it of a blackish brown colour. (Berzelius).

Protosulphuret of lead, PbS , is thrown down from salts of lead as a black precipitate, by sulphuretted hydrogen, which is insoluble in diluted acids or in alkalies. It forms also the ore galena, which crystallizes in the cube and other forms of the regular system; its density is 7.585. Sulphuret of lead is decomposed easily by nitric acid, and converted into nitrate and sulphate of lead, with the separation of a little sulphur. Concentrated and boiling hydrochloric acid dissolves it, with disengagement of sulphuretted hydrogen gas. Galena can be united by fusion with more lead, and gives the subsulphurets Pb_4S , and Pb_2S . When a solution of persulphuret of potassium is added to a salt of lead, a blood red precipitate appears, which is

a persulphuret of lead, but is almost immediately changed into the black protosulphuret of lead and free sulphur.

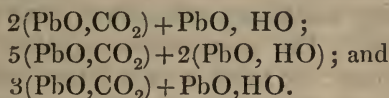
Chloride of lead, Pb Cl , 1737.15 or 139.2.—Lead dissolves slowly in hydrochloric acid, by substitution for hydrogen, forming the chloride of lead. The same compound is obtained by digesting oxide of lead in hydrochloric acid, and also falls as a white precipitate, when a salt of lead is added to any soluble chloride. The chloride of lead is soluble in 135 times its weight of cold water, and more so in hot water, from which it crystallizes in cooling in long flattened acicular crystals, which are anhydrous. The chloride of lead is very fusible, and may be sublimed at a higher temperature. It combines in several proportions with oxide of lead. The *bibasic chloride of lead*, $\text{PbCl} + 2\text{PbO}$, is a colourless crystalline mineral, found at Mendip in Somersetshire. The *tribasic chloride of lead*, $\text{PbCl} + 3\text{PbO} + 4\text{HO}$, is a white insoluble powder that falls when ammonia is added to a solution of chloride of lead. It contains 7 per cent of water (Berzelius). A *surbasic chloride of lead*, $\text{PbCl} + 7\text{PbO}$, is produced on fusing by heat a mixture of 10 parts of pure oxide of lead, and 1 part of pure sal ammoniac, a portion of the lead being at the same time reduced. The surbasic chloride fused affords cubic crystals, on cooling slowly. It forms in that state a beautiful yellow pigment, known as Turner's yellow in this country, and Cassel yellow in Germany. It was prepared in England by digesting litharge with half its weight of common salt, a portion of which is converted into caustic soda, and afterwards washing and fusing the oxichloride formed. But it is sufficient to use 1 part of salt to 7 parts of oxide of lead in this decomposition.

Iodide of lead, Pb I , 2874 or 230.3.—Appears as a beautiful lemon yellow powder, when iodide of potassium is added to a salt of lead. It is soluble in 194 parts of boiling water, and in 1235 parts of water at the usual temperature, and may be obtained from solution in brilliant hexagonal scales of a golden yellow colour. A compound of a paler yellow, which appears in dilute solutions, and when the salt of lead is in excess, is a basic iodide. M. Denot finds three basic iodides of lead, containing to 1 eq. of iodide of lead, 1 eq., 2 eq. and 5 eq. of oxide of lead, and always 1 eq. of water, which last they do not lose below a temperature of about 400° .

Cyanide of lead, Pb Cy , is a white insoluble powder, obtained by precipitation.

Carbonate of lead, Ceruse, White lead; PbO, CO_2 ; 1670.9 or 133.89.—Occurs in nature well crystallized, in the form of carbonate of barytes. It is precipitated as a white powder, of which the grains although very minute are crystalline, when an alkaline carbonate is added to the acetate or nitrate of lead. The precipitate is anhydrous. When oxide of lead is left covered with water in an open vessel, it absorbs carbonic acid, and becomes white, forming the subcarbonate $\text{PbO}, \text{CO}_2 + \text{PbO}, \text{HO}$.

The carbonate of lead is invaluable as a white pigment from its great opacity, which gives it that property, called body by painters, and enables it to cover well. As precipitated by an alkaline carbonate, it is deficient in body, owing to the transparency of the crystalline grains composing the precipitate. It is also a neutral carbonate, as thus prepared, and differs in composition from the ceruse of commerce, which Mulder finds always to contain hydrated oxide of lead in combination with the carbonate of lead. The result of Mulder's analyses of numerous specimens of white lead, is, that there are three varieties of that substance, the composition of which is expressed by the three following formulæ:



Mr. T. Richardson, who has also been engaged with a chemical examination of the varieties of white lead, finds all of them to contain a portion of oxide of lead, in addition to the carbonate, and so far confirms the conclusions of Mulder.*

* The following are Mr. Richardson's results, which he has communicated to me. The specimens were all dried at a temperature of about 300° for 24 hours, previous to analysis. No. 1, was made by the French plan, (by transmitting carbonic acid through subacetate of lead); No. 2 is Kremner white, No. 3, 4, 5, were made by causing small pieces of lead to be agitated in a tub, into which carbonic acid was passed, as practised in London; Nos. 6, 7, 8, 9, 10, were made by the old Dutch plan, but each of the specimens was from a different manufacturer:

	1	2	3	4	5	6	7	8	9	10
Carbonic Acid.	13.70	15.83	13.70	13.03	13.24	14.61	13.71	13.99	12.99	14.95.
Protox. Lead.	86.00	83.49	85.66	85.98	86.46	84.83	86.02	86.09	86.45	85.02.
	99.70	99.32	99.36	99.01	99.70	99.44	99.73	100.08	99.44	99.97.

While the neutral carbonate of lead consists in 100 parts of

Carbonic acid.	.	.	.	16.54
Oxide of lead.	.	.	.	83.46
				100.00

In the old or Dutch mode of preparing white lead, which is still extensively practised, thin sheets of the metal are placed over gallipots containing weak acetic acid (water with about $2\frac{1}{2}$ per cent dry acid), themselves imbedded in fermenting tan, of which the temperature varies from 140° to 150° . The action is often very rapid, and the metal disappears in a few weeks to the centre of the sheet. In this process from two to two and a half tons of lead (4480 to 5600 pounds) are converted into carbonate, by a quantity of vinegar which does not contain more than the small quantity of 50 pounds of dry acetic acid. Hence the metal is certainly neither oxidised nor carbonated in this process, at the expense of the acetic acid. The oxygen must be derived from the air, and the carbonic acid from the fermenting tan. In the newer process, litharge, without any preparation, is mixed with water and about 1 per cent of acetate of lead, and carbonic acid gas sent over it; the oxide of lead is rapidly converted into excellent ceruse. There can be little doubt that all the oxide of lead is successively dissolved by the acetate, and presented to the carbonic acid as a soluble subacetate; a compound which, it is known, absorbs carbonic acid with the greatest avidity, and allows its excess of oxide to precipitate as carbonate of lead. The new process supplies likewise the theory of the old one, the function of the acetic acid being manifestly the same in both processes. Nitrate of lead has been substituted for the acetate, with other things the same as in the last process.

Sulphate of lead; PbO, SO_3 ; 1895.66 or 151.90.—This salt falls when sulphuric acid or a soluble sulphate is added to a solution of acetate or nitrate of lead, as a white dense insoluble precipitate, which appears by the microscope to be composed of minute crystals. Sulphate of lead contains in 100 parts, 26.44 sulphuric acid and 73.56 oxide of lead, and may be exposed to a red heat without decomposition. Mr. Richardson finds that this salt acquires considerable opacity, and may be substituted for ceruse, when prepared in a mode analogous to the new process for that substance; namely by supplying sulphuric acid, in a gradual manner, to a thick mixture of litharge and water, containing a small proportion of acetate of lead. The sulphate of lead may be obtained thus, having any desirable excess of oxide of lead.

Nitrate of lead; PbO, NO_3 ; 2071.53 or 165.99.—Is obtained

by dissolving litharge, at the boiling point, in slightly diluted nitric acid, which should be free from hydrochloric and sulphuric acids. The neutral nitrate crystallizes in large octohedrons, with the secondary faces of the cube, which are sometimes transparent, although generally white and opaque. The crystals are anhydrous; they are soluble in $7\frac{1}{2}$ times their weight of cold, and in much less hot water. The nitrate of lead is decomposed by an incipient red heat, yielding, with oxygen gas, the peroxide of nitrogen, which is prepared in this way, and leaving the yellow oxide of lead. When a small quantity of ammonia is added to nitrate of lead, or when a dilute solution of the neutral salt is boiled with oxide of lead in fine powder, a soluble *bibasic nitrate of lead* is formed $\text{PbO}, \text{NO}_5 + \text{PbO}$. It crystallizes during evaporation in fine scales, or in little opaque grains, which are anhydrous. The granular crystals decrepitate when heated, with extraordinary force. The *tribasic nitrate of lead* precipitates, when ammonia is added in very slight excess to a solution of nitrate of lead. Its constituents are 2NO_5 , 6PbO and 3HO (Berzelius). It is a white powder, which is soluble to a small extent in pure water. When nitrate of lead is digested with a considerable excess of ammonia, the decomposition stops at the point at which 6 eq. of oxide of lead are combined with 1 eq. of nitric acid. The *sexbasic nitrate of lead* contains 2NO_5 , 12PbO and 3HO . (Berzelius).

Nitrites of lead.—When a solution of 100 parts of nitrate of lead is boiled with 78 parts of metallic lead in thin turnings, the lead is dissolved, and a little nitric oxide is evolved, the last being the result of a partial decomposition of nitrous acid previously formed. The solution is alkaline and yellow; and gives, on cooling, brilliant crystalline plates of a golden yellow colour, which are the *bibasic nitrite of lead*, $2\text{PbO} + \text{NO}_3$. By dissolving 100 parts of this salt in water at 167° (75° cent.), and then mixing with the solution 35 parts of oil of vitriol, previously diluted with four times its weight of water, one half of the oxide of lead is precipitated as sulphate of lead, and a solution is obtained of a deep yellow colour, from which the *neutral nitrite of lead*, $\text{PbO}, \text{NO}_3 + \text{HO}$, crystallizes. This salt gives yellow crystals, resembling the nitrate in form. Its solution absorbs oxygen from the air, and like all the nitrites, gives off nitric oxide at 176° (80° cent.), and a subnitrate of lead precipitates. Berzelius, to whom we are indebted for the preceding

facts, also formed a *quadribasic nitrite of lead*, containing NO_3 , 4PbO and HO .

Acetate of lead, $\text{PbO}, (\text{C}_4 \text{H}_3 \text{O}_3) + 3\text{HO}$.—This salt is met with well crystallized, and in a state of great purity in commerce. It is generally prepared by dissolving litharge in the acetic acid procured by the distillation of wood. It crystallizes in flattened four sided prisms, has a taste which is first sweet and then astringent, is very soluble in water, 100 parts of water dissolving 59 of the salt at 60° , and soluble in 8 parts of alcohol. It effloresces in air, and is apt to be decomposed in part by the carbonic acid of the air, and thus to become partially insoluble. It loses the whole of its water when dried at the usual temperature in vacuo. M. Payen crystallized the anhydrous acetate, from solution in absolute alcohol.

Tribasic subacetate of lead, $\text{PbO}, (\text{C}_4 \text{H}_3 \text{O}_3) + 2\text{PbO}$, is formed by digesting oxide of lead in a solution of the neutral salt, till it is strongly alkaline. This salt does not crystallize when so prepared, but may be dried, and then contains no water. It is very soluble, but must be dissolved in distilled water, as the carbonic, hydrochloric and other acids, in well water, precipitate its oxide of lead. M. Payen has observed that the tribasic subacetate crystallizes readily, in fine prismatic needles, when formed by adding ammonia to a moderately strong solution of the neutral acetate. The crystals contain 1 eq. of water, which they lose at 212° . The acetate of ammonia formed at the same time, appears to give stability to the subacetate of lead in solution, and prevents an excess of a whole equivalent of ammonia from throwing down any oxide of lead from the solution. This ammoniacal solution of the subacetate of lead, prepared without an excess of ammonia, is a convenient form in which to apply that salt as a reagent.*

Sesquibasic acetate of lead, $3\text{PbO}, 2(\text{C}_4 \text{H}_3 \text{O}_3) + \text{HO}$.—Was obtained by Payen by adding 3 eq. of the neutral acetate, to a concentrated and boiling solution of 1 eq. of the tribasic nitrate. It is also produced when the neutral and anhydrous acetate of lead is heated in a retort or porcelain capsule, till the whole, after being liquid, becomes a white and porous mass. The sesquibasic acetate is then formed by the decomposition of 3 atoms of neutral acetate of lead, from which there separate

* Mémoire sur les Acetates et le Protoxide de Plomb, par M. Payen, An. de Chim. et de Phys. t. 66, p. 37.

the elements of 1 atom of acetic acid, in the form of carbonic acid and acetone, (Matteucci, Wöhler). This basic salt is very soluble, and crystallizes in plates of a pearly lustre.

A *sexbasic acetate of lead*, 6PbO , $(\text{C}_4\text{H}_3\text{O}_3)$, is formed on dropping a solution of the neutral, or of tribasic acetate of lead, into ammonia in excess. It is a white precipitate, which examined by the microscope, has a crystalline aspect. It contains a little water, which it loses when dried in vacuo.

Alloys of lead.—Lead and tin may be fused together in all proportions. M. Rudberg finds that these metals combine in certain definite proportions having fixed points of congelation :

ALLOYS OF LEAD AND TIN.

1 atom of lead and 3 atoms of tin, congeal at 268.6° .

1 atom of lead and 1 atom of tin, at 464° .

2 atoms of lead and 1 atom of tin, at 518° .

3 atoms of lead and 1 atom of tin, at 536° .

A thermometer placed in a fluid alloy of 1 atom of lead and 2 atoms of tin, becomes stationary when the temperature falls to 392° , a portion solidifies, and a more fusible alloy separates; the temperature again falls, and afterwards becomes stationary at 368.6° , the crystallizing point of the alloy composed of 1 atom of lead, and 3 atoms of tin. If the alloy contains so much tin that its point of complete congelation is under 368.6° , the last compound always separates from it, at that point, and the thermometer remains stationary for a time, whatever may be the proportion of the metals in the alloy.* *Fine solder* is an alloy of 2 parts of tin and 1 of lead; it fuses at about 360° , and is much employed in tinning copper. *Coarse solder* contains one fourth of tin, and fuses about 500° ; it is the substance employed for soldering by plumbers.

Lead, as reduced from the native sulphuret, always contains a little silver. The latter is separated by allowing two or three tons of the melted metal to cool slowly in a hemispherical iron pot; when the lead, as it solidifies, separates in crystals, which can be raked out. The silver remains almost wholly in the more fusible portion, or what may be looked upon as the mother-liquor of these crystals; so that by this operation the argentiferous alloy is greatly concentrated. This mode of

* Rudberg, An. de Chim. et de Phys. t. 48, p. 363.

separation was discovered by Mr. Pattenson of Newcastle. To separate the remaining lead, much of it is converted into massicot, by the action of air upon its surface, in the shallow furnace used for that preparation; and the last portions of lead are removed by continuing the oxidation upon a porous bason or *cupel* of bone-earth, which imbibes the fused oxide of lead, while the melted silver is found in a state of purity upon the surface of the cupel, not being oxidable at a high temperature.

SECTION XI.

BISMUTH.

Eq. 886.9 or 71.07; Bi.

Bismuth generally occurs in the metallic state, and is separated from the gangue or accompanying rock by fusion. It may be prepared in a state of purity, for chemical purposes, by reducing, with charcoal, the oxide of bismuth obtained by igniting the subnitrate.

Bismuth is a white metal of a reddish shade, and highly crystallizable. Its density is 9.53, which may be increased by cautious hammering to 9.8827. It is more fusible than lead, melting at 497°, according to Crichton, and at 507°, according to Rudberg. This metal, like water, expands considerably in crystallizing. It is volatile at a full red heat, and burns in air at a high temperature with a pale blue flame, and the formation of copious fumes of oxide of bismuth. This metal does not oxidate in air; it dissolves with difficulty in boiling hydrochloric or diluted sulphuric acid, by substitution for hydrogen, but is readily oxidised and dissolved by nitric acid. Bismuth resembles several of the magnesian metals, in forming, besides a protoxide, a suboxide of which the composition is unknown, and a peroxide Bi O_2 , which does not combine with acids.

Suboxide of bismuth is formed when the subnitrate is digested in a solution of protochloride of tin, and appears as a black powder, which is soluble with heat in hydrochloric acid, (Vogel). When bismuth is oxidated and fused with metaphosphate of soda upon charcoal, by the blow pipe, and the bead afterwards held in the reducing flame, a colourless glass is obtained, which assumes a black colour on cooling. This is analogous to what

happens with suboxide of copper, and appears to indicate that suboxide of bismuth forms salts, at least in the dry way.

Protoxide of bismuth, BiO ; 986.9 or 79.07; BiO .—Is obtained by the combustion of bismuth, as a straw yellow powder, or by the ignition of the subnitrate. The density of the fused oxide is 8.211. It combines with acids, and forms white salts.

Sulphuret of bismuth, BiS , occurs crystallized, and has, according to Mr. W. Phillips, a form similar to sulphuret of antimony. Hence M. Regnault is disposed to class bismuth with antimony, (An. de Ch. &c. t. 73, p. 70.) The eq. of bismuth would then be multiplied by 3, or made 2660.7, and the protoxide be represented by BiO_3 . Its density is 7.501. The sulphuret is dissolved by the metal in all proportions, by fusion, but separates again when the latter congeals (Lagerhjelm).

Chloride of bismuth, and sulphate of the oxide of bismuth, are formed, by dissolving oxide of bismuth in concentrated hydrochloric and sulphuric acids. They both afford subsalts, when decomposed by water, namely $\text{BiCl} + 2\text{BiO} + \text{HO}$ (Phillips,) and $3\text{BiO} + \text{SO}_3$ (Berzelius). The former is known as *pearl white*. An insoluble *subcarbonate of bismuth* precipitates, on throwing the nitrate into the solution of an alkaline carbonate, which is used in medicine; also a crystalline *tartrate of bismuth*, on adding the nitrate to a solution of Rochelle salt.

Nitrate of bismuth; BiO , $\text{NO}_5 + 3\text{HO}$; 1664 + 337.5 or 133.33 + 27.—This salt is produced when bismuth in powder is thrown into nitric acid, of density 1.42; the action is very violent. Crystals are formed on cooling, which correspond in composition with the magnesian nitrates. This salt is decomposed by heat in the same way as the nitrate of copper, but at a lower temperature, beginning to lose acid in dry air at 80° . Three atoms of the hydrated salt are resolved by heat into 2 atoms of hydrated nitrate of water (acid of sp. gr. 1.42), and 1 atom of subnitrate of bismuth: $3(\text{BiO}, \text{NO}_5 + 3\text{HO}) = 2(\text{HO}, \text{NO}_5 + 3\text{HO})$, and $\text{HO}, \text{NO}_5 + 3\text{BiO}$. The neutral nitrate, and all the soluble salts of bismuth are decomposed by water, which combines with the acid and throws down the oxide, generally in combination with a portion of the acid. Oxide of bismuth must, therefore, be considered as inferior to water, in basic power. The nitrate of bismuth is highly corrosive; it is precipitated as a black sulphuret by sulphuretted hydrogen.

Subnitrate of bismuth, $\text{HO}, \text{NO}_5 + 3\text{BiO}$, mentioned above, is produced at a temperature so low as 180° , and may be exposed to a temperature of 500° without decomposition. At a higher temperature its acid and water go off together. It is the only subnitrate of bismuth ever produced, in the decomposition of the neutral nitrate by heat. When crystals of the neutral nitrate are decomposed by 24 times their weight of water, they give, according to M. Duflos, a hydrated subnitrate containing $\text{NO}_5, 4\text{Bi O}$ and 3HO . This subnitrate, which is used in pharmacy and known as the *magistery of bismuth*, is a brilliant white powder of pearly lustre, composed of microscopic crystalline grains; which is light after being dried, like *magnesia alba*. When prepared by pouring the solution of the neutral nitrate, drop by drop, into a large quantity of water, the composition of the subnitrate is $3\text{BiO} + \text{NO}_5$, according to Mr. Phillips. The subnitrate of bismuth is employed as a cosmetic; it is also used as an internal remedy.

Peroxide of bismuth, Bi O_2 , was formed by Stromeyer by boiling anhydrous protoxide of bismuth finely levigated, with chloride of soda. It is a dark brown anhydrous powder, which gives chlorine with hydrochloric acid, but is not reduced to the state of protoxide by sulphurous acid.

The *alloys of bismuth* are remarkable for their fusibility. The amalgam of this metal is highly liquid. An alloy of 8 parts bismuth, 5 lead and 3 tin melts at 202° ; another mixture of 2 bismuth, 1 lead and 1 tin at $200^\circ.75$, these mixtures are known as fusible metal. Bismuth is also added to the alloy of tin and lead used for casting stereotype plates. Besides increased fusibility, bismuth communicates to this alloy the property of expanding on becoming solid, by which it is calculated to take an accurate impression.

ORDER V.

OTHER METALS PROPER HAVING ISOMORPHOUS RELATIONS WITH
THE MAGNESIAN FAMILY.

SECTION I.

TIN.

Eq. 735.3 or 58.92 ; Sn (stannum).

Tin does not occur native, but its common ore is reduced by a simple process, and mankind appear to have been in possession of this metal from the earliest ages. The most productive mines of tin are those of Cornwall, from which the ancients appear to have derived their principal supply of this metal, and those of the peninsula of Malacca and island of Banca in India.

The only important ore of tin is the peroxide, which is found in Cornwall, both in veins traversing the primary rocks, and in alluvial deposits in their neighbourhood. In the latter case the ore presents itself in rounded grains of greater or less size, which form together a bed covered by clay and gravel. The ore has evidently been removed from its original situation, and the grains rounded by the action of water, which has at the same time divested it of the other metallic ores with which it is accompanied in the vein; these being softer are more easily reduced to powder, and have been carried away by the stream. This ore, called *stream tin*, is easily reduced by coal, and gives the purest tin. The metal from the ore of the veins, is contaminated with iron, copper, arsenic and antimony, from which a portion of it is partially purified by *liquation*. Bars of the impure metal are exposed to a moderate heat, by which the pure tin is first melted, and separates from a less fusible alloy, containing the foreign metals. The purer portion is called *grain tin*, and the other *ordinary tin* or *block tin*. The mass of grain tin is heated till it becomes brittle, and then let fall from a height. By this it splits into irregular prisms, somewhat resembling basaltic columns. This splitting is a mark of the purity of the tin, for it does not happen when the tin is impure.

Pure tin is silver white, very soft, and so malleable, that it may be beaten into thin leaves, tinfoil not being more than 1-1000dth of an inch in thickness. When a bar of tin is bent, it emits a grating sound, which is characteristic; and when bent backwards and forwards rapidly, several times in succession, becomes so hot that it cannot be held in the hand. At the temperature of boiling water, tin can be drawn out into wire, which is very soft and flexible, but deficient in tenacity. The density of pure tin is 7.285, or 7.293 after being laminated; that of the tin of commerce is said to vary from 7.56 to 7.6. Its point of fusion is 442° , both by Crichton and Rudberg; $445^{\circ}.6$ by Kupffer. Tin is volatile at a very high temperature. The brilliancy of the surface of tin is but slowly impaired by exposure to air, and even in water it is scarcely acted upon. Hence the great value of this metal for culinary vessels, and for covering the more oxidable metals, such as iron and copper, when employed as such. Of tin three oxides are known, the protoxide SnO , deutoxide Sn_2O_3 , and peroxide SnO_2 .

Protoxide of tin, Stannous oxide; SnO , 835.3 or 66.92. Tin dissolves in undiluted hydrochloric acid, at the boiling temperature, by substitution for hydrogen, and forms the protochloride of tin. From this the protoxide is precipitated by an alkaline carbonate, as a white hydrate, which may be washed with tepid water and dried at a temperature not exceeding 176° . It does not contain a trace of carbonic acid. This white powder dried more strongly, in a retort filled with carbonic acid, and heated to redness, gives the anhydrous oxide, as a black powder, of which the density is 6.666. In this state the oxide is permanent, but if a body at a red heat is brought in contact with it in open air, it takes fire and burns, and is converted entirely into peroxide. The protoxide of tin dissolves in acids, and with more facility when hydrated than after being ignited. This oxide is also dissolved by potash and soda, but the solution after a time undergoes decomposition; metallic tin is deposited and the peroxide is found in solution. The solution of a stannous salt, and of a stannic salt also, is apt to undergo decomposition, when largely diluted with water, and to deposit a subsalt. The stannous salts absorb oxygen from the air, and have a great affinity for that element; they convert the peroxide of iron into protoxide, and throw down mercury, silver and platinum in the metallic state from their solutions. The chlo-

ride of gold produces a purple precipitate in a stannous salt, consisting, it is believed, of the deutoxide of tin in combination with protoxide of gold, a test by which the protoxide of tin may always be distinguished. The same oxide is precipitated as a black sulphuret, by sulphuretted hydrogen, even from acid solutions.

Protochloride of tin, Salt of tin; $\text{Sn Cl} + 3\text{HO}$; 1178+337.5 or 94.39+27.—This salt may be obtained in the anhydrous state by raising the temperature of a mixture of equal weights of calomel and tin in a gradual manner, and finally distilling the protochloride by a strong red heat. The fused mass on cooling is a grey solid, of considerable lustre, and having a vitreous fracture. The hydrated chloride, known in commerce as salt of tin, is procured by evaporating the solution of tin in concentrated hydrochloric acid to the point of crystallization. It is thus obtained in needles or in larger four sided prismatic crystals, which contain three atoms of water. The salt parts with the greater portion, if not the whole of this water at 212° , but if distilled at a higher temperature, loses hydrochloric acid also, and an oxichloride of tin remains. It dissolves completely in a small quantity of water; but when treated with a large quantity, the salt is partly decomposed, hydrochloric acid is dissolved, and a light milk-white powder separates, which is a basic chloride, or oxichloride, $\text{Sn Cl} + \text{Sn O} + 2\text{HO}$. Both the crystals and the solution absorb oxygen from the air, and then a basic salt of the peroxide is formed which is also insoluble in water. From both these causes, a complete and clear solution of the salt of tin is rarely obtained, unless the water be previously acidulated with hydrochloric acid. This salt is entirely soluble in caustic alkali, but the solution is liable to an ulterior change already mentioned. The protochloride of tin is not only used in calico printing as a mordant, but also as a deoxidising agent, particularly to deoxidise indigo, and to reduce to a lower state of oxidation and discharge the peroxides of iron and manganese fixed upon cloth.

Protochloride of tin and potassium; $\text{Sn Cl} + \text{K Cl}$, and $\text{Sn Cl} + \text{K Cl} + 3\text{HO}$.—The protochloride of tin forms a double salt with chloride of potassium, and also with chloride of ammonium, which crystallize in the anhydrous condition, and also with three atoms of water.

The anhydrous protochloride of tin fused in ammoniacal gas,

absorbs half an equivalent of that gas, according to Persoz, forming $2\text{Sn Cl} + \text{NH}_3$, or probably a double salt like the preceding salt of ammonium, that is, $\text{Sn Cl} + (\text{NH}_3 \text{ Sn}), \text{Cl}$.

Protiodide of tin, Sn I , is formed by heating a mixture of granulated tin and iodine. It was found by Boullay, jun., to form double salts with other iodides, particularly with the iodides of the alkaline and earthy metals, in which two atoms of the stannous iodide are combined with one of the other iodide.

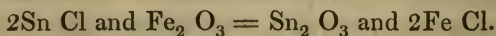
Carbonate of tin.—Carbonic acid does not combine with either of the oxides of tin.

Protosulphate of tin, $\text{Sn O}, \text{SO}_3$.—Tin dissolves in sulphuric acid concentrated or a little diluted, and affords a saline mass, which forms a brown solution in water and deposits small crystalline needles on cooling.

Protonitrate of tin, $\text{Sn O}, \text{NO}_5$, is obtained by dissolving protoxide of tin in nitric acid; the solution cannot be concentrated and is easily altered.

Tartrate of potash and tin, $\text{KO. Sn O} + (\text{C}_8 \text{ H}_4 \text{ O}_{10})$.—Bitartrate of potash dissolves protoxide of tin, and forms a very soluble salt of potash and tin, which, like most of the tartrates, is neither precipitated by caustic alkalies, nor by alkaline carbonates. An addition of bitartrate of potash is occasionally made to the solution of tin used in dyeing.

Deutoxide of tin, $\text{Sn}_2 \text{O}_3$, 1770.6 or 141.88.—Was obtained by M. Fuchs, by diffusing recently precipitated peroxide of iron in a solution of protochloride of tin, containing no excess of acid, and afterwards boiling the mixture. A double decomposition occurs, in which the deutoxide of tin precipitates, and protochloride of iron is retained in solution:



The deutoxide thus obtained is a slimy grey matter, and usually yellow from adhering oxide of iron. Ammonia dissolves it easily, and without a residue, which distinguishes this oxide from the protoxide of tin, the latter being insoluble, or almost so, in that menstruum. The deutoxide of tin is dissolved by concentrated hydrochloric acid; the taste of the solution is not metallic. It is distinguished from a salt of the peroxide of tin, by producing the purple precipitate with chloride of gold. A

sesquisulphuret exists, corresponding with this oxide. The salts of the deutoxide of tin have not been examined.

Peroxide of tin, Stannic oxide, Sn O_2 , 935.3 or 74.92.—This constitutes the common ore of tin, which is generally crystallized. The crystals of *tin stone* are sometimes brownish yellow and translucent, at other times dark brown and almost black, and contain small quantities of protoxides of iron and manganese. Their primitive form is an obtuse octohedron of a square base; their density from 6.92 to 6.96. The peroxide of tin in this state does not dissolve in acids, unless previously ignited with an alkali. Tin is converted into a white powder, which is a hydrated peroxide, by nitric acid; and the acid acts with most violence, when not of its highest degree of concentration. This oxide, after being well washed and dried, contains 11 per cent of water; it reddens litmus paper. After ignition it assumes a pale yellow colour, and is equally insoluble, by the humid way, as the natural oxide.

To prepare the hydrated peroxide of tin, a solution of the bichloride of tin should be precipitated cold, by an alkaline carbonate, and washed with cold water. It forms a white and bulky gelatinous precipitate, which when collected on a filter has a certain degree of transparency. In this condition the peroxide of tin is readily dissolved by hydrochloric acid, whether concentrated or in a diluted state. Dried in vacuo at the usual temperature, it forms hard translucent masses, resembling gum Arabic, which contain not more than 1 eq. of water; and is not changed in properties by the desiccation. If this hydrated oxide be digested in boiling water and collected again on a filter, it is found, without much change in appearance, to be materially altered in properties. The boiled oxide does not dissolve in undiluted hydrochloric acid, but forms with a small portion of it (about 14 per cent) a salt insoluble in an excess of acid. When the excess of acid is decanted, the residue then dissolves in pure water; but it precipitates from the solution when hydrochloric acid is added. If the aqueous solution is boiled, the oxide precipitates; and if the liquor is concentrated, it coagulates like albumen. There can be little doubt that the peculiarities of the boiled oxide are connected with an alteration in its state of hydration. Peroxide of tin, prepared by the action of nitric acid on tin, acquires the same properties, it is to be presumed, from its being exposed to a high temperature in its

formation. The existence of two varieties of the peroxide of tin was observed by Berzelius so early as 1811, and is the first recorded instance of isomerism.

Hydrochloric acid is capable of dissolving a great excess of hydrated peroxide of tin, at least two or three equivalents. The peroxide of tin is also soluble in alkalies; and having in regard to them the powers of a feeble acid, it is sometimes called stannic acid. A very dilute solution of potash boiled with the peroxide of tin, forms a solution in which 1 part of potash may contain 16 parts of peroxide of tin. Peroxide of tin is employed in the preparation of the white glass, known as enamel; and the ignited and finely levigated oxide forms *jeweller's putty*, which is used in polishing hard objects. The hydrated oxide resembles alumina in forming insoluble compounds with the organic colouring matters, and hence its salts are much prized as mordants.

Bisulphuret of tin, Sn S_2 , is precipitated from persalts of tin, of a dull yellow colour, by sulphuretted hydrogen gas. Prepared in the dry way, by igniting a mixture of peroxide of tin, sulphur and sal ammoniac in a covered crucible, it forms the *aurum musivum* or *mosaic gold* of the alchemists. In this operation the sal ammoniac is indispensable, although it seems to serve no other purpose than to prevent the elevation of temperature which results from the sulphuration. Mosaic gold, when well prepared, has the yellow colour of gold, and consists of brilliant translucent scales, which are soft to the touch. No acid dissolves it, except aqua regia. It is decomposed by dry chlorine, and the compound formed, $\text{Sn Cl}_2 + \text{S Cl}_2$ (page 379).

Bichloride of tin, *Permuriate of tin*, Sn Cl_2 ; 1620.6 or 129.86.—The anhydrous bichloride of tin, known as the fuming liquor of Libavius, is procured by distilling, at a gentle heat, a mixture of 4 parts of corrosive sublimate with 1 part of tin in filings, or tin amalgamated with a little mercury and then reduced to powder. A colourless, highly limpid liquid is found in the condenser, which fumes strongly in humid air. The bichloride boils at 248° ; the density of its vapour, observed by Dumas, is 9.1997. It forms a solid saline mass with one third of its weight of water, and dissolves in a larger quantity of water. The same salt is obtained in solution, by conducting a stream of chlorine gas into a strong solution of the protochloro-

ride of tin, till the latter is saturated, which is shewn by the solution ceasing to precipitate mercury from a solution of corrosive sublimate. A solution of this salt, extensively used in dyeing, and known as the nitro-muriate of tin, is generally prepared by oxidising crystallized protochloride of tin by nitric acid; or by dissolving tin in a mixture of hydrochloric and nitric acids, avoiding any considerable elevation of temperature.

Bichloride of tin and ammonia, $\text{Sn Cl}_2 + \text{NH}_3$ or $(\text{NH}_3 \text{ Sn}) \text{Cl}_2$. Anhydrous bichloride of tin absorbs ammoniacal gas, and forms a white powder, which may be sublimed without decomposition; after sublimation it is entirely soluble in water (Rose).

Bichloride of tin, and phosphuretted hydrogen, $3\text{Sn Cl}_2 + \text{PH}_3$. These two bodies unite without the production of hydrochloric acid; the compound is solid (Rose).

Bichloride of tin and potassium, $\text{Sn Cl}_2 + \text{K Cl}$.—The solution of bichloride of tin, when mixed with an equivalent quantity of chloride of potassium and evaporated, yields this double salt in regular octohedrons of a vitreous lustre, which are anhydrous.

A *sulphate and nitrate of peroxide of tin*, have been crystallized; this base forms no carbonate.

Both the *sulphuret* and *bisulphuret of tin* act as sulphur acids, combining with alkaline sulphurets. The bisulphuret of tin dissolves with digestion in sulphuret of sodium, and the concentrated solution yields fine crystals of the salt, $2\text{Na S} + \text{Sn S}_2 + 12\text{HO}$. The bisulphuret of tin is found combined with the subsulphurets of copper and iron, forming *tin pyrites*, a rare mineral, $2\text{Fe}_2 \text{S}, \text{Sn S}_2 + 2\text{Cu}_2 \text{S}, \text{Sn S}_2$.

Alloys of tin.—Tin alloyed with small quantities of antimony, copper, and bismuth, forms the best kind of pewter, which possesses the peculiar whiteness of that metal. The most fusible compound of tin and bismuth, is that of an atom of each metal, Bi Sn ; it melts at 289.4° (Rudberg). When the metals are mixed in other ratios, a portion first congeals at a higher temperature, separating from the compound mentioned, which remains liquid till the temperature falls to 289.4° . Although tin precipitates copper from its solutions in acids, yet it is possible to precipitate tin upon copper, and to cover the latter with tin, as is proved by the tinning of pins. Tin is dissolved in a mixture of one part of bitartrate of potash, two of alum, two of common salt and a certain quantity of water, and

the pins introduced at the boiling temperature. The pins undergo no change in this liquor, supposing it to contain no undissolved tin, but the moment a fragment of tin touches the pins, all those in contact with each other are tinned.

SECTION II.

TITANIUM.

Eq. 303.7 or 24.33; Ti.

This metal was discovered in 1791, by Mr. Gregor of Cornwall, and afterwards by Klaproth who gave it the name titanium. In the form of titanitic acid it constitutes several minerals, as rutile, anatase, menachanite, etc; and as titanate of protoxide of iron, ilmenite and other species.

Titanic acid, mixed with one-sixth of its weight of charcoal powder, may be reduced by the most intense heat of a wind furnace, which does not, however, fuse the titanium. It is frequently found in small cubic crystals of a bright copper colour, on the slag which adheres to the lower part of the iron smelting furnaces. The iron and foreign matter of the slag may be removed by digestion in acids, and the crystals obtained in a separate state. Their density is 5.3; they are harder than quartz. Titanium is not dissolved by any acid, except a mixture of nitric and hydrofluoric acids. It is slowly oxidated in fused nitre. Titanium combines in two proportions with oxygen, forming titanitic oxide TiO , and titanitic acid TiO_2 .

Oxide of titanium, TiO , 403.7 or 32.33.—Is formed when titanitic acid is exposed in a charcoal crucible, to the highest temperature of a wind furnace. Where the acid was in contact with the charcoal, a thin coating of red metallic titanium is formed, but within, it is changed into a black mass, which is insoluble in all acids, and not otherwise affected by them, is oxidated with difficulty when heated in contact with air, or by fusion with nitre. The oxide of titanium is also obtained by the moist way, in the form of a deep purple powder, when a fragment of zinc or iron is introduced into a solution of titanitic acid in hydrochloric acid, but alters so quickly by absorption of oxygen, that an opportunity has not been obtained of studying

its properties. The composition assigned to it above is, therefore, hypothetical.

Titanic acid, TiO_2 , 503.7 or 40.33.—In the mineral rutile, titanic acid is crystallized in the form of tin stone; the link by which tin is connected with titanium. Again ilmenite and other varieties of titanate of iron, FeO , TiO_2 , are isomorphous with peroxide of iron, (page 146); and thus tin comes to be connected through titanium with the last order of metals. But titanic acid is dimorphous, and crystallizes, in anatase, in an unconnected form. Titanic acid is procured more easily from the titanate of iron, reduced to powder and levigated, which is fused with sulphur. The sulphur has no action upon the titanic acid, but converts the protoxide of iron into a sulphuret of iron, which is dissolved by hydrochloric acid. If iron is still retained by the titanic acid, the latter is heated in a stream of sulphuretted hydrogen gas, by which every particle of iron is converted into sulphuret, and then removed by hydrochloric acid.

Titanic acid is a white powder, which acquires a yellow tint by a high temperature; it is infusible and insoluble in water. Titanic acid is considerably analogous in properties to silica; like that acid it has a soluble modification, formed by igniting titanic acid with an alkaline carbonate, which is soluble in dilute hydrochloric acid. The acid solution of titanic acid gives an orange-red precipitate with an infusion of gall-nuts, which is characteristic of titanic acid. On neutralising the acid solution with ammonia, the soluble modification of titanic acid is thrown down as a white gelatinous precipitate. When this precipitate is dried and heated, it glows, and the titanic acid is no longer soluble in acids. When a solution of bichloride of titanium, or of the sulphate of titanic acid in water, is boiled for some time, titanic acid precipitates in the insoluble modification.

Bisulphuret of titanium, Ti S_2 , was discovered by Rose, who formed it by passing the vapour of the bisulphuret of carbon over titanic acid, in a porcelain tube maintained at a bright red heat.

Bichloride of titanium, Ti Cl_2 , was formed by Mr. George of Leeds, by transmitting chlorine over metallic titanium at a red heat. It is a transparent colourless liquid, resembling bichloride of tin, and boiling a little above 212° . The density of its vapour is 6.615 (Dumas). Bichloride of titanium combines with

ammonia, and forms a white saline mass, $\text{Ti Cl}_2 + 2\text{NH}_3$. Metallic titanium is most easily obtained by heating this compound to redness. Bichloride of titanium also absorbs phosphuretted hydrogen, and forms a dry brown powder. From this compound when heated, a lemon yellow sublimate rises, which Rose found to contain 3 atoms of bichloride of titanium, combined with 1 atom of a compound of phosphuretted hydrogen and hydrochloric acid, analogous to sal ammoniac, but which could not be isolated. Bichloride of titanium forms double salts with the alkaline chlorides, which are colourless and capable of crystallizing.

A volatile *bifluoride of titanium*, Ti F_2 , was obtained, by Unverdorben, by distilling titanic acid in a platinum apparatus with fluor spar in powder, and fuming sulphuric acid.

A definite *sulphate of titanic acid*, $\text{TiO}_2 + \text{SO}_3$, is obtained by dissolving titanic acid in sulphuric acid, and evaporating to dryness by a heat under redness.

SECTION III.

CHROMIUM.

Eq. 351.8 or 28.19 ; Cr.

This metal, so remarkable for the variety and beauty of its coloured preparations, was discovered by Vauquelin in 1797, in the red mineral now known as chromate of lead. It has since been found in other minerals, more particularly *chrome iron* ($\text{FeO} + \text{Cr}_2 \text{O}_3$), a mineral which many countries possess in considerable quantity. It is from this ore that the compounds of chromium, used in the arts, are actually derived. The metal may be procured by the reduction of its oxide, in the usual way, but with the same difficulty as manganese. Chromium is a greyish white metal, of density 5.9, fusible with the greatest difficulty, and not magnetic. It does not undergo oxidation in the air; it dissolves in hydrofluoric acid with evolution of hydrogen. Chromium is also obtained as a brown powder, when sesqui-chloride of chromium is heated in ammoniacal gas, (Liebig). Chromium forms two compounds with oxygen, of which the lower, or oxide of chromium, $\text{Cr}_2 \text{O}_3$, is isomorphous

with peroxide of iron and with alumina, and the higher or chromic acid, Cr O_3 , is isomorphous with sulphuric acid.

Oxide of chromium, Cr_2O_3 ; 1003.6 or 80.42.—This oxide exists in chrome iron, but is not immediately derived from that mineral. When chromate of mercury, the orange precipitate obtained on mixing nitrate of mercury and chromate of potash, is strongly ignited, oxide of chromium remains as a powder of a good green colour. The oxide of chromium is also obtained, by deoxidising the chromic acid of bichromate of potash in various ways; by ignition with sulphur, for instance, or by igniting together 1 part of bichromate of potash with $1\frac{1}{2}$ parts of sal ammoniac, and 1 part of carbonate of potash, whereby chloride of potassium and oxide of chromium are formed; the chromic acid losing half its oxygen which is converted into water by the hydrogen of the ammonia. Another process, interesting from affording the oxide in the state of crystals, is to pass the vapour of chloro-chromic acid ($\text{Cr O}_2\text{Cl}$) through a tube heated to whiteness, when oxygen and chlorine gases are disengaged, and oxide of chromium attaches itself to the surface of the tube. The crystals have a metallic lustre, and are of so deep a green as to appear black; they have the same form as specular iron ore, the density 5.21, and are as hard as corundum (Wöhler). The ignited oxide of chromium is not soluble in acids; heated with access of air, and in contact with an alkali, it absorbs oxygen and becomes chromic acid. Fused with borax or other vitreous substances, oxide of chromium communicates to them a beautiful green colour; it is the colouring matter of the emerald, and is employed to produce a green colour upon earthenware. Oxide of chromium (and not chromic acid) is also the colouring matter of *pink colour*, applied to stoneware. This substance is formed by igniting strongly a mixture of 100 parts of peroxide of tin, 33 parts of chalk and not more than 1 part of oxide of chromium.*

To obtain the same oxide in a hydrated condition, a solution of bichromate of potash is brought to the boiling point, and hydrochloric acid and alcohol alternately added in small quantities, till the solution passes from a red to a deep green colour,

* Malaguti, An. de Chim. et de Phys. t. 61, p. 433. Mr. O. Sims finds that peroxides of iron and manganese may be substituted for oxide of chromium in pink colour, so that the coloration of that substance is of an extraordinary character.

and no longer effervesces from the escape of carbonic acid gas, upon the addition of either the acid or alcohol. In this experiment the chromic acid, liberated by the hydrochloric acid, is deprived of half its oxygen by the hydrogen and carbon of the alcohol, and the resulting oxide of chromium is dissolved by the excess of hydrochloric acid present, and in fact converted into the corresponding sesquichloride of chromium. Many other organic substances may be used in place of alcohol in this experiment, such as sugar, oxalic acid, &c. The oxide of chromium is precipitated from the green solution by ammonia, and falls as a pale bluish-green hydrate. The same oxide is obtained more directly, when to a boiling solution of bichromate of potash, a hot solution of the pentasulphuret of potassium is added, the chromic acid then giving half its oxygen to the sulphur.

Hydrated oxide of chromium is soluble in acids, and forms salts. It is also dissolved by potash and soda, but not to a great extent by ammonia. Its solution in acids is generally green or purple by reflected, and red by transmitted light. Its salts have a sweet taste, and are poisonous; they are not affected by sulphuretted hydrogen; alkaline sulphurets precipitate from them the hydrated oxide. The oxide itself becomes of a greener colour when dried, and loses water. A moderate heat affects its relations to acids, the sulphate of the heated (or green) oxide not forming a double salt, for instance, with sulphate of potash. When heated to redness, it glows, or undergoes the same change as zirconia, peroxide of tin, and many other hydrated peroxides when made anhydrous, becomes denser, of a pure green colour, and ceases to be soluble in acids.

A *sesquisulphuret of chromium*, Cr_2S_3 , corresponding with the oxide, is obtained by exposing the latter, in a porcelain tube, to the vapour of bisulphuret of carbon, at a bright red heat. It is a substance of a dark grey colour, which is dissolved by nitric acid.

Sesquichloride of chromium, Cr_2Cl_3 ; 2031.6 or 162.79.—This salt is obtained as a sublimate of a peach-purple colour, when chlorine is passed over a mixture of oxide of chromium and charcoal, ignited in a porcelain tube: or, by evaporating the solution of sesquichloride of chromium to dryness. The salt obtained by the latter process is a green powder, and retains 3HO at 212° ; above 400° it loses water and becomes anhydrous, assuming the same colour as the sublimed chloride. In the anhydrous state it dissolves very slowly in water.

Sulphate of chromium, $\text{Cr}_2\text{O}_3, 3\text{SO}_3$; 2507.1 or 200.90.—Oxide of chromium is dissolved by sulphuric acid, but the salt does not crystallize. When dried strongly, it loses its solubility. It forms, however, a crystallizable double salt with sulphate of potash, *chrome alum*, $\text{KO}, \text{SO}_3 + \text{Cr}_2\text{O}_3, 3\text{SO}_3 + 24\text{HO}$. This salt appears when a mixture of its constituent salts, with a little free sulphuric acid, is left to spontaneous evaporation. Its octohedral crystals are of a dark purple colour, and of a beautiful ruby red, when so small as to be transparent. The solution of chrome alum is bluish purple, but when heated to 140° or 180° becomes green, a change of colour which indicates the decomposition of the salt; for when afterwards evaporated, it no longer yields crystals of chrome alum, but of sulphate of potash, and the sulphate of chromium dries up into a gummy mass. Iron alum is often decomposed in the same manner, by heating its solution, and is not reproduced on cooling. The best mode of preparing chrome alum is to mix three parts of a saturated solution of neutral chromate of potash, first with one part of oil of vitriol, and then with two parts of alcohol, which is added by small portions to the mixture of acid and chromate, and not to apply artificial heat. The chromic acid is thus deoxidised in a gradual manner, and large crystals of the double sulphate are slowly deposited, (Fischer.)

Oxalate of chromium and potash, $3(\text{KO}, \text{C}_2\text{O}_3) + \text{Cr}_2\text{O}_3, 3\text{C}_2\text{O}_3 + 6\text{HO}$.—This is another beautiful double salt of chromium. It is easily prepared by the following process of Dr. Gregory. One part of bichromate of potash, two parts of binoxalate of potash, and two of crystallised oxalic acid are dissolved together in hot water. A copious evolution of carbonic acid gas takes place, arising from the deoxidation of the chromic acid, at the expense of a portion of the oxalic acid, and nothing fixed remains, except the salt in question, of which a pretty concentrated solution crystallizes upon cooling in prismatic crystals, which are black by reflected light, but of a splendid blue by transmitted light, when sufficiently thin to be translucent. The oxide of chromium cannot be precipitated from this salt completely by an alkaline carbonate; and it is remarkable that only a small portion of the oxalic acid is thrown down from it by chloride of calcium. When fully dried and then carefully ignited, this salt is completely decomposed, and leaves a mixture of chromate and carbonate of potash. The corresponding

double oxalate of chromium and soda contains 9HO, according to Mitscherlich. In the analogous oxalate of peroxide of iron and soda, the proportion of water appeared to me to be 10HO.

The mineral *chrome iron*, $\text{Fe O, Cr}_2 \text{O}_3$, crystallizes in octohedrons, and corresponds with the magnetic oxide of iron, having the peroxide of iron replaced by oxide of chromium. Its density is 4.5; it is about as soft as felspar, and infusible. When exposed to long continued calcination, in contact with carbonate of potash, in a reverberatory furnace, the oxide of chromium of this compound absorbs oxygen, and combines as chromic acid with the potash, while the protoxide of iron becomes peroxide. The addition of nitre increases the rapidity of oxidation, but is not absolutely required in the process. A yellow alkaline solution of carbonate and chromate of potash is obtained by lixiviating the calcined matter, which is generally converted into the red chromate or bichromate of potash, by the addition of the proper quantity of sulphuric acid, the latter salt being more easily purified by crystallization than the neutral chromate.

Chromic acid, Cr O_3 , 651.8 or 52.19.—This acid is not liberated from the chromates in a state of purity by any acid except the fluosilicic; it is also easily altered. Fluosilicic acid gas is conducted into a warm solution of bichromate of potash, till the potash is completely separated as the insoluble fluoride of silicon and potassium, which may be ascertained by testing a few drops of the solution with tartaric acid or chloride of platinum. The solution is evaporated to dryness by a steam heat, and the chromic acid redissolved by water; it gives an opaque dull red solution. Chromic acid may also be obtained anhydrous and in acicular crystals, by distilling, in a platinum retort, a mixture of 4 parts of chromate of lead, 3 parts of finely pulverised fluor spar, and 7 parts of the Nordhausen sulphuric acid; sulphate of lime is formed, and the superfluoride of chromium, the vapour of which is received in a large platinum crucible, covered by wet paper, and used as a condenser. The superfluoride is decomposed by the aqueous vapour from the paper, being resolved into hydrofluoric acid and beautiful orange-red acicular crystals of chromic acid, which fill the crucible. Chromic acid differs remarkably from sulphuric acid, in having but little affinity for basic water, so that it may be obtained anhydrous by evaporating its solution to dryness. Indeed, the chromate of water is not known to exist, even in combination, both the

bichromate and terchromate of potash being anhydrous salts. The free acid is a highly oxidating agent, and bleaches organic colouring matters: chromic acid then loses half its oxygen, and becomes oxide of chromium. When sulphurous acid is transmitted through the solution of a chromate, a brown precipitate subsides, which is a subchromate of the oxide of chromium. The same compound frequently appears when chromic acid is otherwise imperfectly deoxidised.

CHROMATES.

Chromate of potash, Yellow chromate of potash, KO, CrO_3 ; 1241.7 or 99.5.—This salt is produced in the treatment of the chrome ore, but is seldom crystallized. It may be formed from the bichromate, by fusing that salt with an equivalent quantity of carbonate of potash; or by adding caustic potash to a red solution of the bichromate, till its colour becomes a pure golden yellow. The solution of chromate of potash has a great tendency to effloresce upon the sides of the bason when evaporated. Its crystals are of a yellow colour, anhydrous, and isomorphous with sulphate of potash. One hundred parts of water at 10° dissolve $48\frac{1}{3}$ parts of this salt; the solution preserves its yellow colour, even when diluted to a great degree.

Bichromate of potash, Red chromate of potash, $\text{KO}, 2\text{CrO}_3$; 1893.5 or 151.73.—This beautiful salt, of which a large quantity is consumed in the arts, crystallizes in prisms, or in large four-sided tables, of a fine orange red colour. It fuses under a red heat, and forms a crystalline mass on cooling, of which the crystals have the same form as those obtained from an aqueous solution, according to Mitscherlich; but this mass falls to powder as it cools, from the unequal contraction of the crystals in different dimensions. At 60° , water dissolves 1-10th of its weight of this salt, and at the boiling point a considerably greater quantity.

Bichromate of chloride of potassium, Peligot's salt, $\text{KCl} + 2\text{CrO}_3$.—This salt, which we are obliged to designate as if it contained chloride of potassium in combination as a base with chromic acid, is formed by dissolving together with the aid of heat, about three parts of bichromate of potash and four of concentrated hydrochloric acid, with a small quantity of water, avoiding the evolution of chlorine. It crystallizes in flat red quadrangular prisms, and is decomposed by solution in pure water.

Terchromate of potash, $\text{KO}, 3\text{Cr O}_3$, is obtained crystallized when a solution of the bichromate is mixed with nitric acid, and evaporated. Bichromates of soda and of silver exist, which are anhydrous, like the bichromate of potash, (Warington.)

Chromate of soda, $\text{Na O}, \text{Cr O}_3 + 10\text{HO}$.—By the evaporation of a concentrated solution of this salt, it is obtained in large fine crystals, having the form of glauber salt.

Chromate of lead, $\text{PbO}, \text{Cr O}_3$; 2046.3 or 163.97.—This compound, so well known as *chrome yellow*, is obtained by mixing the nitrate, or acetate of lead, with the chromate or bichromate of potash. The precipitate is of a lighter shade from dilute than from concentrated solutions. It is entirely soluble in potash or soda, but not in dilute acids.

Subchromate of lead, $2\text{Pb O}, \text{Cr O}_3$, is of a red colour. It is formed when a solution of neutral chromate of potash, with as much free alkali added to it as it already contains, is added to a solution of nitrate of lead. But the finest vermilion-red subchromate is formed when one part of the neutral chromate of lead is thrown into five parts of nitre, in a state of fusion by heat. Water dissolves the chromate and nitrate of potash of the fused mass, and leaves the subchromate of lead, as a crystalline powder, (Liebig and Wöhler.) An orange pigment may be obtained very economically by boiling the sulphate of lead, which is a waste product in making acetate of alumina from alum by means of acetate of lead, with a solution of chromate of potash. The subchromate of lead forms a beautiful orange upon cloth, which is even more stable than the yellow chromate, not being acted upon by either alkalies or acids. One method of dyeing chrome orange, is to fix the yellow chromate of lead first in the calico, by dipping it successively in acetate of lead and bichromate of potash, and then washing it. This should be repeated, in order to precipitate a considerable quantity of the chromate in the calico. A milk of lime is then heated in an open pan, and when at the point of ebullition, the yellow calico is immersed in it, and instantly becomes orange, being deprived of a portion of its chromic acid by the lime, which forms a soluble chromate of lime. At a lower temperature, lime-water dissolves the chromate of lead entirely, and leaves the cloth white.

Chromate of silver falls as a reddish brown precipitate when nitrate of silver is added to neutral chromate of potash. Dissolved in a hot and concentrated solution of ammonia, it gives,

on cooling, large well formed crystals, Ag O , $\text{Cr O}_3 + 2\text{NH}_3$, isomorphous with the analogous ammoniacal sulphate and seleniate of silver.

Chromate of magnesia forms, according to my own observations, yellow crystals which are very soluble, and contain 5HO . It does not form a double salt with chromate of potash, as sulphate of magnesia does with sulphate of potash. It is remarked that the insoluble metallic chromates generally carry down portions of the neutral precipitating salts, or of subsalts, and their analysis is often unsatisfactory from that cause. When the magnesian chromates are compared with the sulphates of the same family, the former are found to have their water readily replaced by metallic oxides, but not by salts; so that subchromates with excess of oxide are numerous, while few or no double chromates exist.

Chlorochromic acid, $\text{Cr O}_2 \text{Cl}$, or $2\text{Cr O}_3 + \text{Cr Cl}_3$.—This is a volatile liquid, obtained by distilling, in a glass retort, by a gentle heat, 3 parts of bichromate of potash and $3\frac{1}{2}$ parts of common salt, previously reduced to powder and mixed together, with 5 parts by water measure, of oil of vitriol, discontinuing the distillation when the vapours, from being a deep orange red, become pale—that change arising from watery vapour. The compound is a heavy red liquid, decomposed by water. The density of its vapour is 5.9

Terfluoride of chromium, Cr F_3 , is obtained in the manner already mentioned under the preparation of chromic acid. It is a blood-red liquid. No corresponding terchloride of chromium has been obtained in an isolated state.

SECTION IV.

VANADIUM.

Eq. 856.9 or 68.66; V.

Vanadium, so named from *Vanadis*, a Scandinavian deity, was discovered by Sefström in 1830, in the iron prepared from the iron ore of Taberg, in Sweden, and procured afterwards in larger quantity from the slag of that ore. It was found afterwards by Mr. Johnston, in a new mineral discovered by him, the vanadate of lead from Wanlockhead. It is one of the rarest of the elements. The metal itself has considerable re-

semblance in properties to chromium. It combines with oxygen in three proportions, forming the protoxide of vanadium, VO , peroxide, VO_2 , and vanadic acid, VO_3 .

Protoxide of vanadium, VO , 956.9 or 76.66, is produced by the action of charcoal or hydrogen upon vanadic acid. It is a black powder of semi-metallic lustre, and when made coherent by pressure, conducts electricity like a metal. It does not combine with acids, and exhibits none of the characters of an alkaline base. It is readily oxidised when heated in the open air, and passes into the following compound.

Peroxide of vanadium, VO_2 , 1056.9 or 84.66—is produced by the action of sulphuretted hydrogen and other deoxidating substances upon vanadic acid. When pure, it is a black pulverulent substance, quite free from any acid or alkaline reaction. It dissolves in acids, and forms salts, most of which are of a blue colour. These salts give a precipitate with a slight excess of carbonate of soda, of a greyish white hydrate, which becomes red by oxidation. They are also precipitated black by infusion of nutgalls, like the salts of iron. Peroxide of vanadium is also capable of acting as an acid, and forms compounds with alkaline bases, some of which are crystallizable.

Vanadic acid, VO_3 ; 1156.9 or 92.66.—It is in this state that vanadium occurs in the slag of the iron of Taberg, and in the vanadate of lead. It is obtained by dissolving the latter mineral in nitric acid, and precipitating the lead and arsenic, with which the vanadium is accompanied, by sulphuretted hydrogen. A blue solution of peroxide of vanadium remains, which becomes vanadic acid when evaporated to dryness. Vanadic acid fuses but retains its oxygen at a strong red heat. It is very sparingly soluble, water taking up only 1-100th of its weight of this compound, acquiring a yellow colour and an acid reaction. It acts the part of a base to stronger acids. An interesting double phosphate of silica and vanadic acid was observed in crystalline scales, of which the formula is $2\text{SiO}_3, \text{PO}_5 + 2\text{VO}_3, \text{PO}_5 + 6\text{HO}$. Vanadic acid forms with bases neutral and acid salts, the first of which admit of an isomeric modification, being both white and yellow, while the acid salts are of a fine orange red. Vanadic and chromic acids are the only acids of which the solution is red, while they are distinguished from each other by the vanadic acid becoming blue, and the chromic acid green, when they are deoxidised.

Sulphurets and chlorides of vanadium, corresponding with the peroxide and vanadic acid, have likewise been formed.*

SECTION V.

TUNGSTEN AND MOLYBDENUM.

TUNGSTEN.

Syn. WOLFRAM. *Eq.* 1183 or 94.8; W.

This element exists in the form of tungstic acid in several minerals, of which the most important are the native *tungstate of lime* CaO, WO_3 , and *wolfram*, or the tungstate of manganese and iron, $\text{MnO}, \text{WO}_3 + 3(\text{FeO}, \text{WO}_3)$. Its name tungsten means in Swedish, *heavy stone*, and is expressive of the great density of its preparations.

Tungstic acid parts with oxygen easily, and may be reduced in a glass tube, by means of dry hydrogen gas, at a red heat. The metal is thus obtained in the state of a dense dark grey powder, which it is necessary to expose to a very violent heat to fuse into globules, for tungsten is even less fusible than manganese. The metal, when fused, has the colour and lustre of iron, and is not altered in air: it is, after gold and platinum, the densest of the metals, the specific gravity of tungsten being from 17.22 to 17.6. When heated to redness, in the pulverulent form, it takes fire, burns, and becomes tungstic acid. Tungsten forms two compounds with oxygen, tungstic oxide, WO_2 and tungstic acid, WO_3 .

Tungstic oxide, WO_2 , 1383 or 110.8.—This oxide is obtained as a brown powder when tungstic acid is reduced by hydrogen at a temperature not exceeding low redness. Tungstic acid may also be deprived of oxygen in the humid way, by pouring diluted hydrochloric acid over it, and placing zinc in the liquor; the tungstic acid then gradually changes into tungstic oxide, in the form of brilliant crystalline plates of a copper-red colour. No saline compounds of this oxide with acids are known. When digested in a strong solution of hydrate of potash, it dissolves, with the disengagement of hydrogen gas, and the formation of tungstate of potash.

* Berzelius, An. de Ch. et de Ph. t. 47, p. 337.

A compound of tungstic oxide and soda, $\text{Na} + \text{O}_2\text{WO}_2$, of a very singular nature, was discovered by Wöhler. It is obtained by adding to fused tungstate of soda as much tungstic acid as it will take up, and exposing the mass at a red heat to hydrogen gas. After dissolving out the neutral undecomposed tungstate by water, the new compound remains in golden yellow scales and regular cubes, possessing the metallic lustre and a striking resemblance to gold. This compound is not decomposed by aqua regia, sulphuric or nitric acid, nor by alkaline solutions, but yields to hydrofluoric acid. It cannot be prepared by uniting soda directly with tungstic oxide.

Tungstic acid, WO_3 ; 1483 or 118.8—is most conveniently obtained by decomposing the native tungstate of lime, finely pulverised, by hydrochloric acid; chloride of calcium is dissolved, and tungstic acid precipitates. Dissolved in ammonia and precipitated again by acids, tungstic acid always forms a compound with the acid employed. It may be obtained in a separate state by heating the tungstate of ammonia to redness. It is an orange yellow powder, which becomes dull green when strongly heated. Its density is 6.12. It is quite insoluble in water or in acids, but dissolves in alkaline solutions.

Tungstic acid forms both neutral and acid salts with the alkalies. The *tungstate of potash* is a very soluble salt, which may be obtained in small crystals by the evaporation of its solution. When a little acid is added to the solution, an acid salt precipitates, which is very slightly soluble in water. The *tungstate of soda* is also very soluble, but may be obtained in good crystals, which contain a large quantity of water of crystallization. The acid tungstate of soda is very crystallizable, and soluble in eight parts of water. A combination of tungstic acid with tungstic oxide, WO_2, WO_3 , is obtained as a fine blue powder when the tungstate of ammonia is heated to redness in a retort, and is also produced in other circumstances. Malaguti is disposed to consider this compound as a distinct acid of tungsten, W_2O_5 (An. de Ch. et de Ph. lx. 271.)

Sulphurets of tungsten.—The bisulphuret is prepared by mixing one part of tungsten with six parts of cinnabar, and exposing the mixture, covered with charcoal in a crucible, to a white heat. The tersulphuret is formed by dissolving tungstic acid in an alkaline sulphuret, and precipitating by an acid. It is of a liver-brown colour, and becomes nearly black on drying.

The tersulphuret of tungsten has a certain degree of solubility in water containing no saline matter, and is a strong sulphur acid. The salt KS, WS_3 forms pale red crystals. Two parts of this sulphur salt dissolved in water with one part of nitre, give large and beautiful ruby-red crystals of a double salt, $\text{KS}, \text{WS}_3 + \text{KO}, \text{NO}_5$.

Bichloride of tungsten, WCl_2 , is formed when metallic tungsten is heated in chlorine gas. It condenses in dark red needles, which are very fusible and volatile. This chloride is decomposed by water, and tungstic oxide with hydrochloric acid formed.

Terchloride of tungsten, WCl_3 , is produced at the same time as the last compound, and also when the sulphuret of tungsten is heated in chlorine gas. It forms a sublimate of beautiful red crystals, which are resolved by water into tungstic and hydrochloric acids. A *chlorotungstic acid*, or double compound of terchloride of tungsten and tungstic acid, WO_2Cl , or $\text{WCl}_3 + 2\text{WO}_3$, is prepared by heating tungstic oxide in chlorine gas. It condenses in yellow crystalline scales : when suddenly heated, it is resolved into tungstic acid, bichloride of tungsten, and chlorine. Another compound is known, $2\text{WCl}_3 + \text{WO}_3$ (Bonnet.)

MOLYBDENUM.

Eq. 598.5 or 47.96, Mo.

This metal is closely allied to tungsten. Its native sulphuret was first distinguished from plumbago by Scheele, in 1778 ; and a few years afterwards, molybdic acid, which he had formed, was reduced, and molybdenum obtained from it, by another Swedish chemist, Hjelm. The name molybdenum is derived from the Greek term for plumbago.

The oxides of molybdenum are easily reduced, when exposed to a strong heat in a crucible lined with charcoal, but the metal itself is very refractory. Bucholz, who obtained it in rounded buttons, found it to be a white metal, of density between 8.615 and 8.636. It is not acted upon by hydrochloric, hydrofluoric, or diluted sulphuric acid ; but is dissolved by concentrated sulphuric acid, by nitric acid, and aqua regia. Hydrate of potash does not dissolve this metal by the humid way. It combines in three proportions with oxygen, forming molybdous oxide, MoO , molybdic oxide, MoO_2 , and molybdic acid, MoO_3 .

Molybdous oxide, MoO , 698.5 or 55.96.—This oxide is obtained by adding to the concentrated solution of any molybdate, so much hydrochloric acid as to redissolve the molybdic acid which is at first thrown down, and placing zinc in the liquid; this becomes first blue, then reddish-brown, and finally black, and contains the chloride of zinc and protochloride of molybdenum. To separate the oxide of molybdenum from the oxide of zinc, ammonia is added to the liquid in quantity no more than sufficient to precipitate the former, while the latter remains in solution. The molybdous oxide carries down with it a portion of oxide of zinc, from which it may be freed by washing with ammonia: it is thus obtained as a hydrate of a black colour. The hydrate of molybdous oxide dissolves with difficulty in acids, forming solutions which are almost black and opaque, and which do not yield crystallizable salts. It is not dissolved by potash, nor by the fixed alkaline carbonates; but, on the contrary, is soluble in carbonate of ammonia, when freshly precipitated. Molybdous oxide resists, after ignition, the action of all acids.

Molybdic oxide, MoO_2 ; 798.5 or 63.96.—This oxide may be obtained by igniting molybdate of ammonia in a covered crucible, but mixed with a little molybdic acid. It is better procured by igniting rapidly, in a covered crucible, a mixture of anhydrous molybdate of soda (which may contain an excess of soda) with sal ammoniac. Water poured upon the fused mass dissolves common salt, and leaves a brown powder almost black. But molybdic oxide prepared in this way is insoluble in acids. The hydrated oxide may be obtained in various ways, one of which consists in digesting molybdic acid with hydrochloric acid and copper, till all the molybdic acid is dissolved. From the solution, which is of a deep red colour, molybdic oxide is precipitated in appearance exactly similar to the hydrated peroxide of iron, by ammonia, added in sufficient excess to retain all the oxide of copper in solution. The hydrate has a certain degree of solubility in pure water, and should, therefore, be washed with a solution of sal ammoniac, and lastly by alcohol. This hydrate reddens litmus paper, but possesses no other property of an acid. It is not dissolved by the hydrated alkalies, but is soluble in their carbonates, like several earths and metallic oxides. It dissolves in acids and forms salts, which are red when they contain water of crystallization, and black when an-

hydrous. The oxalate of molybdic oxide can be obtained in crystals by spontaneous evaporation.

Molybdic acid, MoO_3 ; 898.5 or 71.96.—The native sulphuret of molybdenum, in fine powder, is roasted in an open crucible, with constant stirring, at a heat not exceeding low redness, so long as sulphurous acid comes off. It leaves a dull yellow powder, which is impure molybdic acid. This is dissolved in ammonia, and the molybdate of ammonia purified by evaporation, during which some foreign matters are deposited, and crystallized. The crystallized salt, exposed to a moderate heat, so as to avoid fusion, loses its ammonia, and leaves molybdic acid in a state of purity. The acid thus prepared is a white and light porous mass, which may be diffused in water, and divides into little crystalline scales of a silky lustre. It fuses at a red heat, and forms on cooling a straw-coloured crystalline mass, of which the density is 3.49. This acid forms no hydrate. It requires 570 times its weight of water to dissolve it. Before being ignited, it is soluble in acids, and forms a class of compounds, in which it appears to play the part of base, but of which not much is known. When boiled with bitartrate of potash, molybdic acid dissolves, even after being fused by heat.

When a solution of bichloride of molybdenum is poured into a solution saturated, or nearly so, of molybdate of ammonia, a blue precipitate falls, which is a *molybdate of molybdic oxide*, $\text{Mo}_2, 2\text{Mo}_3$. This compound is likewise readily formed in a variety of other circumstances.* The salts of molybdic acid are colourless, when their base is not coloured. When they are treated with other acids, molybdic acid precipitates, which dissolves, however, in an excess of the acid, except in nitric acid. It forms both neutral and acid salts with the alkalies. *Molybdate of potash* is formed by dissolving molybdic acid in carbonate of potash; it is easily soluble in water and crystallizable. *Molybdate of soda* has the same form, and resembles in properties the tungstate of soda. *Bimolybdate of soda* crystallizes in large fine crystals, which effloresce in air. *Molybdate of magnesia* is soluble in twelve or fifteen times its weight of water, and may be crystallized. *Molybdate of lead* occurs finely crystallized

* It will be observed, that the atom of this compound contains *three* atoms of metal, so also does the remarkable combination of tungstic oxide and soda, (page 618); both thus containing a *sal*-molecule of metal, like the compound oxide of iron, which appears to be a condition of stability.

as a mineral. Chromate of lead is dimorphous, and corresponds in the least usual of its forms with molybdate of lead: hence molybdenum is connected with the magnesian metals, and tungsten also with the same class, from the isomorphism of the tungstates and molybdates.

Sulphurets of molybdenum.—The *bisulphuret* is the ore from which the compounds of this metal are derived. It occurs in many parts of Sweden, and might be procured in quantity if any useful application of the metal were discovered. It is a lead-grey mineral, having the metallic lustre, composed of flexible laminae, soft to the touch, and making a streak upon paper, like plumbago. Nitric acid oxidates it easily, without dissolving it. Its density is from 4.138 to 4.569. A *tersulphuret of molybdenum* is obtained in the same way as the corresponding compound of tungsten, and affords crystallizable sulphur salts, which are red. The sulphomolybdate of sulphuret of potassium combines likewise with nitrate of potash. When a solution of the former salt is boiled with tersulphuret of molybdenum in excess, the latter is converted into bisulphuret of molybdenum, and a *quadrisulphuret of molybdenum* dissolves in combination with the sulphuret of potassium. The quadrisulphuret may be precipitated by hydrochloric acid, and when dried is a cinnamon brown powder.

Chlorides of molybdenum.—A *protochloride* is formed when molybdous oxide is dissolved in hydrochloric acid; the *bichloride* when molybdenum is heated in dry chlorine gas, as a dark-red gas, which condenses in crystals, like those of iodine. It forms a crystallizable double salt with sal ammoniac. The *chloromolybdic acid*, or compound of terchloride of molybdenum and molybdic acid, MoO_2Cl or $\text{MoCl}_3 + 2\text{MoO}_3$, is formed with molybdic acid, when molybdic oxide is exposed to chlorine gas at a red heat. It sublimes under a red heat, and condenses in crystalline scales, which are white with a shade of yellow.

SECTION VI.

TELLURIUM.

Eq. 801.8 or 64.25; Te.

Tellurium is a metal of rare occurrence, and appeared at one time to be almost confined to certain gold mines in Transyl-

vania ; but it has been found lately, in considerable abundance, at Schemnitz, in Hungary, combined with bismuth ; and in the silver mine of Sadvinski in the Altai, united with silver and with lead. It was first described as a new metal by Klaproth, who gave it the name tellurium, from *tellus*, the earth. Tellurium is separated from the foreign bodies with which it is mixed and combined in its ores, by processes of a very complicated nature. (Berzelius, *Traité*, I. 344.)

In a state of purity, tellurium is silver-white and very brilliant. It is very crystallizable, assuming a rhombohedral form, in which it is isomorphous with arsenic and antimony. It is brittle, and an indifferent conductor of heat and electricity for a metal. Its density is from 6.2324 to 6.2578, according to Berzelius. Tellurium is about as fusible as antimony ; at a higher temperature it may be distilled. It burns in air, at a high temperature, with a lively blue flame, green at the borders, and diffuses a dense white smoke, which generally has the odour of decaying horse-radish, from the presence of a little selenium. Tellurium belongs to the sulphur class of elements. Like selenium and sulphur, it dissolves to a small extent in concentrated sulphuric acid, and communicates to it a fine purple red colour. In this solution, the metal is not oxidated, for it is precipitated again, in the metallic state, by water. This metal has also considerable analogy with antimony, and may probably connect together the sulphur and phosphorus families. Tellurium combines in two proportions with oxygen, forming tellurous acid, TeO_2 , and telluric acid, TeO_3 .

Tellurous acid, TeO_2 ; 1001.8 or 80.25.—This acid differs remarkably in properties according as it is anhydrous or hydrated, forming two isomeric modifications of the same acid, of which the anhydrous acid has been named alphetellurous acid, and the hydrated betatellurous, by Berzelius, to whom we are indebted for nearly all our accurate knowledge of the acids of tellurium. But a sufficient distinction will be made between these bodies by retaining one of these terms, alphetellurous, as applied to the anhydrous acid, and confining the term tellurous acid to the hydrated acid. The proper tellurous acid then is obtained by precipitating the bichloride of tellurium by cold water ; or by fusing anhydrous tellurous acid with an equal weight of carbonate of potash, so long as carbonic acid is disengaged, dissolving the tellurite of potash in water, and adding nitric acid

to it, till the liquor distinctly reddens litmus paper. A white and bulky precipitate is produced, which is washed with ice-cold water, and afterwards dried without artificial heat. Tellurium likewise dissolves with violence in pure nitric acid of density 1.25, and if after the first five minutes, the clear liquid be poured into water, tellurous acid is precipitated in white flocks. But if not immediately precipitated, the nitric acid solution undergoes a change.

The hydrated acid obtained by these processes forms a light, white, earthy mass, of a bitter and metallic taste. It instantly reddens litmus paper, and while still humid, dissolves to a sensible extent in water. It is very soluble in acids, and these solutions are not subject to change, except that in nitric acid. Ammonia and the alkaline carbonates also dissolve it easily, the latter becoming bicarbonates. It is this tellurous acid which plays the part of acid in the tellurites, and also that of base in some compounds which the tellurous, like vanadic, tungstic, and molybdic acids, forms with the stronger acids. The tellurites of potash and soda, which are neutral in composition, are very soluble, and have a strong alkaline reaction; their solutions are decomposed by the carbonic acid of the air.

Alphatellurous acid.—When the solution of tellurous acid in water is heated to 104° , it deposits alphetellurous acid in grains, and loses its acid reaction. The same change occurs when it is attempted to dry the hydrated tellurous acid by heat. It parts with combined water, and becomes granular. The solution of tellurous acid in nitric acid changes spontaneously in a few hours, and in a quarter of an hour when heat is applied to it, and allows the alphetellurous acid to precipitate. When the deposition of the acid is slow, it forms a crystalline mass of fine grains, among which octohedral crystals may be perceived by the microscope. The acid is then anhydrous. Alphetellurous acid does not redden litmus, or not till after a time. It is but very slightly soluble in water; the solution has no acid reaction. No salts of alphetellurous have been formed in the humid way, although from its analogy to a corresponding telluric acid, it is probable that such salts may exist. At a low red heat, it fuses into a clear transparent liquid of a deep yellow colour, which on cooling becomes a white and highly crystalline mass, easily detached from a crucible. Tellurous acid is volatile, although less so than the metal itself.

Bitellurite of potash, $\text{KO}, \text{Te}_2\text{O}_4$, is obtained by fusing two atoms of tellurous acid with one atom of carbonate of potash. It appears to be capable of existing in a hot solution, and of crystallizing in certain circumstances; but it is decomposed by cold water, which resolves it into the neutral salt, which dissolves, and a *quadritellurite of potash*, $\text{KO}, \text{Te}_4\text{O}_8 + 4\text{HO}$. The latter salt cannot be redissolved again in water, without decomposition. In losing its water when heated, it swells up like borax.

Telluric acid, TeO_3 ; 1101.8 or 88.25.—This acid is obtained in combination with potash, on fusing tellurous acid with nitre. It may then be transferred to barytes, and the insoluble tellurate of barytes decomposed by sulphuric acid. The solution of telluric acid gives bulky hexagonal prismatic crystals. Its taste is not acid, but metallic, resembling that of nitrate of silver. Indeed, it appears to be a feeble acid, reddening litmus paper, although with difficulty, when the solution is diluted. The crystallized acid contains 3HO , of which it loses 2HO by efflorescence, a little above 212° . It thereafter appears insoluble in cold water, but may be redissolved completely by long digestion, particularly with ebullition, and is not permanently altered. Telluric affects the same multiples in its salts as tellurous acid. The neutral *tellurate of potash* is $\text{KO}, \text{TeO}_3 + 5\text{HO}$, *bitellurate of potash*, $\text{KO}, \text{Te}_2\text{O}_6 + 4\text{HO}$, *quadritellurate of potash*, $\text{KO}, \text{Te}_4\text{O}_{12} + 4\text{HO}$. All these salts may be obtained directly, in the humid way, by dissolving the proper proportions of hydrated acid and carbonate of potash together, in hot water. A portion of the combined water, in the last two salts, is unquestionably basic, but how much of it is so has not been determined. They cannot be made anhydrous by heat without being essentially altered in properties.

Alphatelluric acid.—The crystals of hydrated telluric acid lose all their water at a heat under redness, and become a mass of a fine orange yellow colour, without changing their form. This yellow matter, which is distinguished as alphatelluric acid by Berzelius, is remarkable for its indifference to chemical reagents, being completely insoluble in cold or boiling water, in hot hydrochloric and nitric acids, and in potash ley. At a high temperature it is decomposed, losing oxygen, and leaving tellurous acid white and pulverulent. The salts of telluric acid are also converted into tellurites, at a red heat, by the loss of oxygen.

The neutral tellurate of potash undergoes no change in constitution under the influence of heat, resembling in that respect those tribasic phosphates, of which the whole three atoms of base are fixed. The bitellurate of potash loses its water and becomes yellow at a temperature under redness, and is changed into a quadritellurate, which is insoluble alike in water and dilute acids. Water dissolves out neutral tellurate from the yellow mass. The insoluble salt is named the alphasquadritellurate of potash, by Berzelius. The elements of this compound are united by a powerful affinity. It is formed when hydrated telluric acid is mixed intimately with another potash salt, such as nitre or chloride of potassium, and the mixture calcined at a temperature which should be much inferior to a red heat; also when tellurous acid is ignited with chlorate of potash, and in other circumstances. Hydrate of potash dissolves the alphasquadritellurate by fusion, and nitric acid by a long continued ebullition; but in both cases the acid is found as ordinary telluric acid in solution.

Telluretted hydrogen, TeH , is a gaseous compound of tellurium and hydrogen, analogous in constitution and properties to sulphuretted hydrogen. It is obtained by fusing tellurium with zinc or with tin, and acting on the mixture by hydrochloric acid.

Definite *sulphurets of tellurium* have been obtained, corresponding with tellurous and telluric acids. They are sulphur acids.

Two *chlorides of tellurium* have been formed, a protochloride, TeCl , to which there is no corresponding oxide, and a bichloride, TeCl_2 . No higher chloride, corresponding with telluric acid, has been obtained.

ORDER VI.

METALS ISOMORPHOUS WITH PHOSPHORUS.

SECTION I.

ARSENIC.

Eq. 940.1 or 75.34 (470.04 or 37.67, *Berzelius and Turner*), As.

This metal is found native, but more generally in combination with other metals, particularly cobalt and nickel, and is largely condensed, during the roasting of their ores, in the state of arsenious acid. The metal may be easily obtained, in a state of purity, by subliming a portion of native arsenic in a glass tube or retort, by the heat of a lamp, or by reducing a mixture of one part of arsenious acid and three parts of black flux, in the same apparatus. The metal forms a crust, in condensing, of a steel-grey colour and bright metallic lustre. It has been observed to crystallize by sublimation in rhombohedral crystals, and is isomorphous with tellurium and antimony. It is a brittle metal, and very easily pulverised. The density of arsenic is from 5.7 to 5.96. It rises in vapour at 356° (180° Cent.) without first undergoing fusion. Arsenic vapour is colourless; its density is 10,370; and, like phosphorus and oxygen, its combining measure is one volume. It has as strong an effect upon the organ of smell as selenium: its odour resembles that of garlic. Arsenic combines in three proportions with oxygen, forming a grey suboxide by spontaneous oxidation in air, of which the composition is undetermined, with arsenious and arsenic acids, As O_3 and As O_5 .

Arsenious acid, As O_3 ; 1240.1 or 99.34.—This compound is also known as white oxide of arsenic, and is an abundant mercantile product. It is in vitreous masses, as obtained by sublimation, which immediately after sublimation are transparent and colourless, or have a delicate shade of yellow, but gradually become white and opaque, (page 153.) The density of the vitreous acid is 3.7385, of the opaque acid, 3.699. Arsenious acid sublimates at 380° , without softening or fusing, forming a vapour which is colourless and without odour. The density of

this vapour is about 13,000 (Mitscherlich); one volume of arsenious acid vapour, or the combining measure, contains accordingly, one volume of arsenic vapour and three volumes of oxygen gas. When slowly sublimed in a glass tube, it is always obtained in distinct transparent crystals of adamantine lustre, which are regular octohedrons. But arsenious acid is dimorphous, and occurs sometimes, in the roasting of arsenical ores, in thin, flexible prisms, of a pearly lustre, of which the form does not belong to the regular system, (Wöhler.) Arsenious acid dissolves very slowly in water, and the prismatic crystals in particular require to be heated with it for a long time. A concentrated solution prepared in this way may afterwards be cooled without arsenious acid immediately crystallizing from it. One hundred parts of boiling water dissolve 9.68 parts of the vitreous acid, and 11.47 parts of the opaque acid; and when the solutions cool to 60° , 1.78 parts remain in the first, and 2.9 parts in the latter; the first reddens litmus paper, the second makes it blue, although feebly, if already red. When the vitreous acid in powder, is covered with ammonia, it heats a little; no combination of the acid with ammonia takes place, for the latter may be completely removed by water, but the washed powder is found to have passed into the condition of the opaque acid. For these curious facts we are indebted to M. Guibourt. The taste of powdered arsenious acid is scarcely perceptible, but it is slightly sweet, and leaves a feeling of acidity in the mouth.

Arsenious acid dissolves in the solutions of many acids, particularly hydrochloric acid, to a greater extent than in water, but without combining with these acids. It is dissolved, however, by the bitartrate of potash, with the formation of a crystallizable salt, analogous to the potash-tartrate of antimony. Arsenious acid is dissolved by potash, soda, and ammonia; but the salts which it forms with these bases do not crystallize. It is also dissolved by alkaline carbonates, but is sometimes deposited from these solutions in a free state; so that it is doubtful whether arsenious acid displaces carbonic acid in the humid way. The arsenites of the earths and metallic oxides are insoluble in water, but soluble in acids; these precipitated arsenites usually carry down an excess of arsenious acid, and are not easily obtained in a definite state.

Arsenic acid, AsO_5 , 1440.1 or 115.34.—This acid is obtained

by heating powdered arsenious acid in a bason, with an equal quantity of water, and adding to the mixture at the boiling point nitric acid in small quantities, so long as ruddy fumes escape. An addition of hydrochloric acid to the water is generally made, to increase the solubility of the arsenious acid, but it is not absolutely necessary. The solution of arsenic acid is then evaporated to dryness, to expel the remaining nitric and hydrochloric acids, but the dry mass is not heated above the melting point of lead, otherwise oxygen gas is emitted and arsenious acid reproduced. Arsenic acid, thus obtained, is milk-white, and contains no water. Exposed to air, it slowly deliquesces, and runs into a liquid. But notwithstanding this, when strongly dried, it does not dissolve completely in water at once, and a portion of it appears to be insoluble; but the whole is dissolved by continued digestion. Arsenic acid, in absorbing moisture from the air, sometimes forms hydrated crystals, which are highly deliquescent; but this acid is easily made anhydrous, and does not retain basic water with force, like phosphoric acid. Its solution has a sour taste, and reddens vegetable blues. Arsenic acid, indeed, is a strong acid, and expels, with the aid of heat, all the volatile acids from their combinations. Arsenic acid undergoes fusion at a red heat, and is completely dissipated in arsenious acid and oxygen at a higher temperature.

When an equivalent of arsenic acid is ignited with an excess of carbonate of soda, three equivalents of carbonic acid are expelled, and a tribasic arseniate of soda formed, which crystallizes when dissolved in water, with 24 equivalents of water, forming the salt $3\text{NaO}, \text{AsO}_5 + 24\text{HO}$, isomorphous with the subphosphate of soda. The same salt is obtained by treating arsenic acid in solution, with an excess of caustic soda. When carbonate of soda is added to a hot solution of arsenic acid, so long as there is effervescence, a salt is obtained by evaporation, corresponding with the common phosphate of soda, containing 2 eq. of soda and 1 eq. of water as bases. This salt affects the same two multiples, in its water of crystallization, as phosphate of soda, namely 24HO and 14HO , but most frequently assumes the smaller proportion, forming the salt $2\text{NaO}, \text{HO}, \text{AsO}_5 + 14\text{HO}$. This arseniate is more soluble than the phosphate, and slightly deliquescent in damp air. When to the last salt a quantity of arsenic acid is added, equal to what it already

contains, and the solution is highly concentrated, the salt named binarsenate of soda crystallizes at a low temperature. This salt contains 1 eq. of soda, and 2 eq. of water as bases, with 2 eq. of water of crystallization, and corresponds with the biphosphate of soda. Its formula is $\text{NaO}, 2\text{HO}, \text{AsO}_5 + 2\text{HO}$. The binarsenate of potash, which is analogous in composition, is a highly crystallizable salt. It is sometimes prepared by deflagrating arsenious acid, with an equal weight of nitrate of potash. These arseniates of the alkalies, which contain water as base, all lose that element at a red heat, but unlike the phosphates they recover it, when again dissolved in water. Arsenic acid, therefore, forms only one, and that a tribasic class of salts. The arseniates of earths and other metallic oxides are insoluble in water, but soluble in acids. The arseniate of silver ($3\text{AgO}, \text{AsO}_5$) falls as a precipitate, of a chocolate brown colour, when nitrate of silver is added to the solution of an arseniate, and affords an indication of the presence of arsenic acid.

Sulphurets of arsenic.—When the following sulphuret, realgar, is digested in caustic potash, it loses sulphur and leaves a brownish black powder, having some resemblance to peroxide of lead, which is the sulphuret SAs_6 , according to Berzelius. *Bisulphuret of arsenic*, AsS_2 , is obtained by fusing sulphur with an excess of arsenic or arsenious acid. It is transparent and of a fine ruby colour after cooling, and may be distilled without decomposition. It forms the crystalline mineral realgar. *Sulpharsenious acid* or *orpiment*, AsS_3 , also occurs native. It may be prepared by decomposing a solution of arsenious acid in hydrochloric acid, by sulphuretted hydrogen, or by an alkaline sulphuret. This sulphuret has a rich yellow colour, and is the basis of the pigment king's yellow. It is insoluble in acids, but is soluble to a small extent in water, containing sulphuretted hydrogen, and also in pure water, but is precipitated by ebullition with a little hydrochloric acid. When heated it fuses readily, and becomes crystalline on cooling. It is readily dissolved by ammonia and solutions of the fixed alkalies, and is indeed a powerful sulphur acid. *Sulpharsenic acid*, AsS_5 , falls as a yellow precipitate, having very much the appearance of orpiment, when a solution of arsenic acid, somewhat concentrated, is decomposed by sulphuretted hydrogen. It may be sublimed without change; and gives a mass after cooling, which is not crystalline.

Chlorides of arsenic.—A *terchloride*, As Cl_3 , corresponding with arsenious acid, is formed when arsenic is introduced into chlorine gas, in which it takes fire and burns spontaneously. The same compound is obtained by distilling a mixture of 1 part of arsenic, with 6 parts of corrosive sublimate, as a colourless, oily, and very dense liquid. It is resolved by water into arsenious and hydrochloric acids. A lower chloride of arsenic appears to be formed when a mixture of arsenic and calomel is distilled; it is obtained as a dark brown sublimate, mixt with calomel. No chloride corresponding with arsenic acid is known. The *bromide of arsenic*, As Br_3 , is formed by the direct combination of its elements. The *iodide of arsenic*, As I_3 , is formed, according to Plisson, by digesting 3 parts of arsenic with 10 of iodine, and 100 of water, so long as the odour of iodine is perceived. The liquid yields by evaporation red crystals of the iodide. The *fluoride of arsenic* is obtained by the distillation of a mixture of fluor spar and arsenious acid with sulphuric acid. It is a fuming colourless liquid; the density of its vapour is 2730 (Unverdorben).

Arsenic and hydrogen.—A solid arseniuret of hydrogen was obtained, by Davy, by using metallic arsenic as the negative pole (the chloroid), in decomposing water. Gay-Lussac and Thenard have also shewn that the same compound precipitates, when arseniuret of potassium is dissolved in water. It is a chestnut brown powder, which may be dried without change. Its composition is not certainly determined. *Arsenietted hydrogen*, As H_3 , a gas analogous in constitution to ammonia, is obtained by dissolving an alloy of equal parts of zinc and arsenic in sulphuric acid, diluted with three times its weight of water. It is a dangerous poison, when inhaled even in the most minute quantity, and should, therefore, be prepared with the greatest caution. The density of this gas is 2695, according to M. Dumas. It is liquefied by a cold of -40° . When passed through a glass tube, heated to redness by a spirit lamp, this gas is decomposed and deposits metallic arsenic. The flame of this gas, when burned in air, also deposits metallic arsenic upon a cold object exposed to it. No combination of arsenietted hydrogen is known with either acids or bases. It precipitates many of the metallic solutions, which are precipitated by sulphuretted hydrogen, but not oxide of lead; its hydrogen alone being oxidated by the common metallic oxides, and the arsenic

precipitating in combination with the metal. This gas, when pure, is completely absorbed by a solution of sulphate of copper, and As Cu_3 precipitated.

TESTING FOR ARSENIC.

Poisoning from arsenious acid is greatly more frequent than from any other substance. Hence, a more than usual degree of importance is attached to the modes of detecting the presence of arsenic in minute quantity. Of the different preparations of the metal, arsenic acid, and after it arsenious acid, are the most poisonous; the salts and sulphurets are so to a much less degree. Arsenious acid in the solid form and unmixed with foreign matters, is easily recognised as a white heavy powder, which is tasteless or nearly so, is entirely volatile by heat, and diffuses a garlic odour in the reducing flame of a lamp. When in solution in water, arsenious acid may be detected by fluid tests, of which the three following are the most important.

1. *Sulphuretted hydrogen gas*, made to a stream through a solution of arsenious acid, produces a precipitate of orpiment, or a golden yellow solution if the quantity of arsenic be very small. In this experiment, the liquid should always be slightly acidulated with hydrochloric or nitric acid, and also be boiled, afterwards, to complete the precipitation of the sulphuret.

2. *Ammonio-nitrate of silver*, is an exceedingly delicate test of arsenious acid, whether free, or in combination with an alkali. This reagent is prepared by adding diluted ammonia to a solution of nitrate of silver, till the oxide of silver, which is first thrown down, is again redissolved. When the ammonia has been added in proper quantity and not in excess, the odour of that substance is scarcely perceptible, and the liquid contains in solution the crystallizable ammonio-nitrate of silver, $\text{Ag O,NO}_5 + 2\text{NH}_3$. This test liquid throws down from arsenious acid, the yellow arsenite of silver, which is redissolved both by acids and ammonia. A solution of nitrate of silver gives the same indication, as the prepared ammonia-nitrate, in an alkaline, but not in an acid solution of arsenious acid. Nitrate of silver produces a yellow precipitate of phosphate of silver, in phosphate of soda or any other soluble phosphate, of the same colour as the arsenite of silver, and which might, therefore, be mistaken for the latter. But the action of the am-

monio-nitrate is not liable to that ambiguity, as it does not produce a yellow precipitate in an alkaline solution of phosphoric acid; the phosphate of silver being then retained in solution by the ammonia of the reagent, although arsenite of silver is precipitated in the same circumstances. Both phosphate and arseniate of silver are indeed considerably more soluble in ammonia, than the arsenite of the same metal.

3. *Ammonio-sulphate of copper*, gives a beautiful green precipitate, the arsenite of copper, in both alkaline and acid solutions of arsenious acid; sulphate of copper gives the same precipitate in the former, but not in the latter.

But in solutions containing organic matter, the indications of these tests are sometimes delusive, and often doubtful, particularly the indications of the latter two. Recourse is then had to the proper means of obtaining arsenic in the metallic form, in which it cannot be mistaken, from the liquid suspected to contain arsenious acid. Indeed, even where the indications of the fluid tests are clear, the reduction test should never be omitted, the evidence which it affords being of a superior and completely demonstrative character. The reduction test of arsenic is practised in two different ways: (1) by the reduction of the sulphuret of arsenic by means of charcoal and carbonate of potash, and (2) by the production, and subsequent decomposition of the gaseous compound of arsenic and hydrogen. The following operations are necessary in the practice of the first method:

REDUCTION TEST OF ARSENIC.

I. Preparation of the fluid:

1. Boil the matters with water and a few drops of nitric acid.
2. Strain through calico.
3. Precipitate animal matter by an excess of nitrate of silver, and subsequent addition of common salt.
4. Filter through paper.

II. Precipitation of the sulphuret of arsenic:

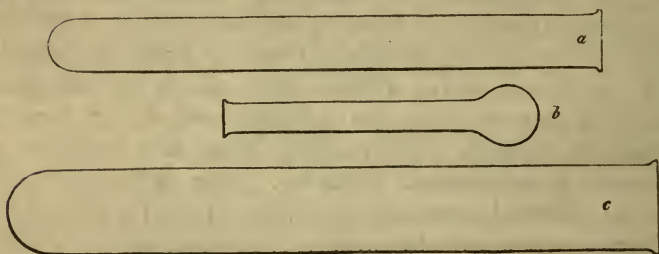
1. Transmit a stream of sulphuretted hydrogen through the liquid for half an hour.
2. Heat the liquid in an open vessel for a few minutes, to cause the precipitate to separate.

3. Wash the precipitate by affusion of water acidulated with hydrochloric acid, and subsidence.
4. Dry the precipitate at a temperature not exceeding 300°.

III. Reduction of the sulphuret of arsenic :

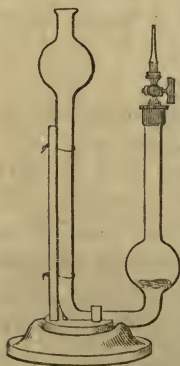
1. Mix the dried precipitate intimately with twice its bulk of dry black flux (carbonate of potash and charcoal), and heat to redness in a glass tube, of the form and size of *a* or *b*, exhibited below.
2. Heat slowly a particle of the metallic crust in a glass tube *c*, and observe the formation of a white crystalline sublimate of arsenious acid.

FIG. 82.



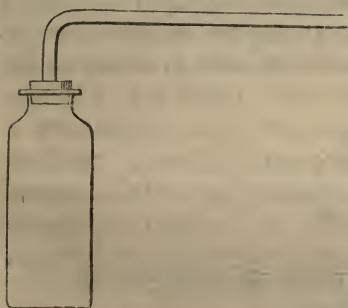
Hydrogen cannot be evolved in contact with a soluble or insoluble preparation of arsenic, without combining with the metal, which is thus removed from the liquor, in the form of arseniatted hydrogen gas. Mr. Marsh has founded, upon that fact, a simple and elegant mode of obtaining metallic arsenic from arsenical liquors. The stopcock being removed from the

FIG. 83. bulbed apparatus represented in the figure, a fragment of zinc is placed in the lower bulb, and diluted sulphuric poured upon it. The stopcock being replaced and closed, the lower bulb is soon filled with hydrogen gas, and the acid liquid forced into the upper bulb. It is necessary to test this hydrogen for arsenic, which will be found in it, if the zinc itself contains that metal. The gas for this purpose is kindled at the stopcock and allowed to burn with a small flame. If a stoneware plate be depressed upon the flame, a black spot of a steel-grey colour and bright metallic lustre,



is formed upon the surface of the plate, in a few seconds, supposing the gas to contain arsenic, or if a cold object of glass be held over the flame, at a small height above it, a white sublimate of arsenious acid condenses upon the glass. But if the zinc employed contains no arsenic, neither of these effects is produced. The zinc being proved to be free from arsenic, a portion of the liquor to be tested, is introduced into the lower bulb, in addition to the acid and zinc already there; and when the bulb comes again to be filled with hydrogen gas, the latter is burned and examined precisely as before. If the liquor is loaded with organic matter, as generally happens with the liquids submitted to examination in actual cases of poisoning, the gas may be filled with froth, and the evolution of it very slow. But in the course of a night, the gas is generally obtained in sufficient quantity, and in a proper state, to permit of an examination of it. Where the gas is evolved freely and without frothing of the liquid, a plain bottle with a cork and glass jet will be sufficient for this reduction experiment. Then also instead of burning the gas at the jet, it may be allowed to escape by a horizontal tube,

FIG. 84.



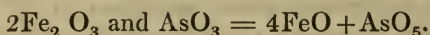
such as that in the figure, a portion of which is heated to redness by a spirit lamp; the arsenic condenses within the tube, beyond the flame and nearer the aperture, and forms a metallic crust. Or the extremity of this tube may be allowed to dip in a solution of nitrate of silver, by which the arseniетted hydrogen is condensed, and a black bulky precipitate of arseniuret of silver

formed. This precipitate, when dried and heated in a glass tube, affords a white sublimate of arsenious acid, which may afterwards be dissolved by boiling in a small quantity of distilled water, containing a single drop of ammonia, and the solution tested for arsenious acid by nitrate of silver and sulphate of copper. (Liebig, Clark).

When the liquid examined contains antimony, that metal combines with the nascent hydrogen, and comes off as antimonietted hydrogen, a gas which when burned, or when heated in a glass tube, gives the metal and a white sublimate, in the same

circumstances as arsenic, (L. Thompson.) Antimony, however, may be recognized by a peculiarity of its reduction in the ignited tube. This metal is deposited in the tube, on both sides of the heated portion of it, and closer to the flame than arsenic, owing to the less volatility of antimony. The white sublimate also, if dissolved in water containing a drop of ammonia, will not give the proper indications with the fluid tests of arsenic, if the metal is antimony.

Antidote to arsenious acid.—When hydrated peroxide of iron is mixed with a solution of arsenious acid to the consistence of a thin paste, a reaction occurs by which the arsenious acid disappears in a few minutes, and the mass ceases to be poisonous. The arsenious acid derives oxygen from the peroxide of iron, and becomes arsenic acid, while the peroxide of iron becomes protoxide, a protarsenate of iron being the result, which is insoluble and inert :



The constitution of this arseniate of iron is probably $2\text{FeO} \cdot \text{HO} \cdot \text{AsO}_5 + 2\text{FeO}$. Peroxide of iron, when used as an antidote to arsenious acid, should be in a gelatinous state as it is obtained by precipitation, without drying. It may be prepared extemporaneously, by adding bicarbonate of soda in excess to any tincture, or red solution of iron.

SECTION II.

ANTIMONY.

Eq. 1612.9 or 129.24 ; (806.4 or 64.62 *Berzelius and Turner*) ;
Sb (*stibium*).

This metal was well known to the alchemists, and is one of the metals of which the preparations were first introduced into medicine. Its sulphuret is not an uncommon mineral, and is the source from which the metal and its compounds are always derived.

The sulphuret of antimony is easily reduced to the metallic state by mixing together 4 parts of that substance, 3 parts of crude tartar and $1\frac{1}{2}$ parts of nitre, and projecting the mixture by small quantities at a time into a red hot crucible. The sulphuret is also sometimes reduced by fusion with small iron nails,

which combine with the sulphur and disengage the antimony. Or it may be obtained in a state of greater purity, by igniting strongly in a crucible, a quantity of the potash-tartrate of antimony, and placing the metallic mass obtained, in water, to remove any potassium it may have acquired. Antimony is a white and brilliant metal, generally possessing a highly lamellated structure. It is easily obtained in rhombohedral crystals of the same form as arsenic and tellurium. Its density is from 6.702 to 6.86. It undergoes no change in the air. The point of fusion of antimony is estimated at 797° ; it may be distilled at a white heat. This metal burns in air at a red heat, and produces copious fumes of oxide of antimony. Antimony combines in three proportions with oxygen, forming oxide of antimony and antimonious acid, SbO_3 and SbO_5 , which correspond respectively with arsenious and arsenic acids, and antimonious acid SbO_4 , which is probably an intermediate or compound oxide, analogous to the black oxide of iron.

Oxide of antimony; Sb O_3 , 1912.9 or 153.28.—Oxide of antimony may be obtained by dissolving the sulphuret finely pounded, and in the condition in which it is known as prepared sulphuret of antimony, in four times its weight of concentrated hydrochloric acid. Pure sulphuretted hydrogen comes off, and the antimony is converted into terchloride (Sb S_3 and $3\text{H Cl} = \text{Sb Cl}_3$ and 3HS .) The clear solution may be poured off, and precipitated at the boiling point by a solution of carbonate of potash, added in excess; the carbonic acid, which does not combine with oxide of antimony, escapes as gas. Oxide of antimony so prepared, is anhydrous, but is slightly soluble in water; it is white, but assumes a yellow tint when heated. It is fusible at a red heat, and sublimes at a high temperature in a close vessel, where it cannot pass into a higher state of oxidation. The brilliant crystalline needles which condense about antimony in a state of combustion are likewise this oxide. They possess the unusual prismatic form of arsenious acid observed by Wöhler. Oxide of antimony also crystallizes as frequently in regular octohedrons, the other form of arsenious acid. It occurs in the prismatic form, as a rare mineral, of which the density is 5.227.

When a solution of potash is poured upon the bulky hydrate of oxide of antimony, which is precipitated from the chloride by water, a portion of the oxide is dissolved, but the greater

part loses its water, and is reduced in a few seconds to a fine greyish, crystalline powder, which is a neutral combination of the oxide of antimony with potash. Oxide of antimony enters into other salts as a base.

Sulphuret of antimony, Sb S_3 , 2216.4 or 177.6.—The common ore of antimony is a tersulphuret, Sb S_3 , corresponding with the preceding oxide of antimony. It is rarely free from sulphuret of arsenic, which thus often enters the antimonial preparations derived from the sulphuret of antimony, but into tartar emetic less frequently than the others. The same sulphuret is formed when salts of the oxide of antimony, such as tartar emetic, are precipitated by sulphuretted hydrogen, but it is then of an orange red colour. When the precipitated sulphuret is dried, it loses water and becomes anhydrous, still remaining of a dull orange colour; but heated more strongly, it shrinks at a particular temperature, and assumes the black colour and metallic lustre of the native sulphuret. This sulphuret is also obtained of a dark brown colour by boiling the prepared sulphuret of antimony in a solution of carbonate of potash, and allowing the solution to cool; by fusing $2\frac{2}{3}$ parts of the prepared sulphuret with 1 part of carbonate of potash, or dissolving it in a boiling solution of caustic potash, and afterwards adding an acid. This preparation is known as *Kermes mineral*. It has a much duller colour than the precipitated sulphuret, but differs from it only in containing a small quantity of an alkaline sulphuret, which cannot be removed by washing (Berzelius). When the sulphuret of antimony is oxidated at a red heat, much sulphur is burned off, and an impure oxide of antimony remains. This matter forms, when fused, the *glass of antimony*, which contains a considerable quantity of undecomposed sulphuret. The glass reduced to powder is boiled with bitartrate of potash, as a source of oxide of antimony, in the pharmaceutical preparation of tartar emetic. The oxide of antimony is dissolved out from the glass by acids, and a substance is left which is called *saffron of antimony*. This last is a definite compound of oxide and sulphuret of antimony, $\text{Sb O}_3 + 2\text{Sb S}_3$, which also occurs as a mineral, namely red antimony ore.

Chloride of antimony, Sb Cl_3 , is obtained by distilling either metallic antimony or the sulphuret of antimony with corrosive sublimate. When heated it flows like an oil, and becomes a

crystalline mass on cooling. It is a powerful cautery. This salt deliquesces in air, and is troubled, owing to the deposition of a subsalt. A concentrated solution of chloride of antimony is also obtained by dissolving the sulphuret of antimony in hydrochloric acid. When this solution is thrown into water, it gives a white, bulky precipitate, which after a time resolves itself into groups of small crystals, having usually a fawn colour; it was formerly called the *powder of Algaroth*. These small crystals are an oxichloride of antimony, of which the composition is $2\text{Sb Cl}_3 + 9\text{Sb O}_3$, according to the analysis of Johnston and Malaguti.

Sulphate of antimony, $\text{Sb O}_3, 3\text{SO}_3$, is obtained by boiling metallic antimony with concentrated sulphuric acid, as a white saline mass, which is decomposed by water.

Oxalate of potash and antimony, $\text{KO, C}_2\text{O}_3 + \text{Sb O}_3, 3\text{C}_2\text{O}_3$.—This is a double crystallizable salt of antimony, which, like the tartrate of potash and antimony, may be dissolved in water without decomposition. It is prepared by saturating binoxalate of potash with oxide of antimony. It is soluble, at 48° , in ten times its weight of water, (Lassaigne.) According to Bussy, when binoxalate of potash is digested upon oxide of antimony in excess, two salts are formed, one in oblique prisms, and another less soluble, in intricate small crystals; but neither is very stable. The former is decomposed by much water: its analysis gave $3(\text{KO, C}_2\text{O}_3) + \text{Sb O}_3, 3\text{C}_2\text{O}_3 + 6\text{HO}$.*

Tartrate of potash and antimony, $\text{KO. Sb O}_3 + (\text{C}_8 \text{H}_4 \text{O}_{10}) 2\text{HO}$; $4164.2 + 225$ or $333.68 + 18$.—This salt, the tartar emetic or potash tartrate of antimony of pharmacy, is prepared by neutralising bitartrate of potash with oxide of antimony; the oxide obtained by decomposing the chloride or sulphate of antimony with water answers best for the purpose. A quantity of oxide of antimony may be boiled with three or four times its weight of water, and bitartrate of potash added in small quantities till the oxide is entirely dissolved. The filtered solution yields the salt, on cooling, in large transparent crystals, of which the form is an octohedron with a rhombic base; they become white in the air, and lose their water of crystallization. They are soluble in 14 times their weight of cold water, and in 1.88 boiling water, but not in alcohol. The mother liquor of these crystals becomes a syrupy liquid, and dries up into a gummy mass

* Journal de Pharm. 1838, p. 509.

without crystallizing, when oxide of antimony has been dissolved in excess by the acid tartrate, in preparing the salt. Oxide of antimony is precipitated by potash or ammonia from a solution of this salt, when concentrated, but not when diluted, owing to the solubility of oxide of antimony in alkalis. Salts of the earths and basic metallic oxides, such as barytes and oxide of silver, throw down from its solution a compound of the tartrate of antimony, with tartrate of barytes, tartrate of silver, &c (Wallquist.) Strong acids decompose the salt, and produce a precipitate which is a mixture of bitartrate of potash with oxide of antimony, or with a subsalt of that oxide. Sulphuretted hydrogen gas throws down the orange red sulphuret of antimony from a solution of the tartrate, and this precipitate affords the most conclusive indication of the presence of antimony. The orange precipitate should be collected, dried, and dissolved by heat in a few drops of concentrated hydrochloric acid. When the acid solution is dropped into a glass of water, the white and bulky hydrated oxichloride of antimony precipitates.

This salt was formerly described as a double tartrate of potash and antimony, or, abstracting its water of crystallization, which is differently stated at 2 and 3 equivalents, as $\text{KO}, (\text{C}_4\text{H}_2\text{O}_5) + \text{SbO}_3, (\text{C}_4\text{H}_2\text{O}_5)$. When the atomic weight of tartaric acid is doubled, and it is represented as a bibasic acid, the formula for dry tartar emetic becomes $\text{KO} \cdot \text{SbO}_3, (\text{C}_8\text{H}_4\text{O}_{10})$. In comparing the last formula with that of bitartrate of potash, represented also as a bibasic salt, $\text{KO} \cdot \text{HO}, (\text{C}_8\text{H}_4\text{O}_{10})$, it is observed that 1 eq. of oxide of antimony takes the place of 1 eq. of water, as base, although the former contains three eq. of oxygen and the latter only one. Tartrate of potash and antimony is, in this respect, an anomalous salt. Another equally remarkable fact respecting this salt has been observed by M. Dumas, namely, that 2 eq. of water are separated from the anhydrous salt at 428° , leaving a substance of which the elements are, $\text{C}_8\text{H}_2\text{O}_{12}\text{SbK}$. The first part of this formula $\text{C}_8\text{H}_2\text{O}_{12}$, M. Dumas looks upon as a quadribasic salt-radical existing in the tartrates, which in hydrated tartaric acid is united with 4H, in bitartrate of potash with $3\text{H} + \text{K}$, and in tartrate of antimony and potash with $\text{Sb} + \text{K}$. Here Sb is found equivalent to, and capable of replacing 3H, (note p. 542). Tartrate of antimony and potash would, therefore, fall to be represented by $\text{K Sb}, (\text{C}_8\text{H}_2\text{O}_{12}) + 2\text{HO} + \text{water of crystallization}$.

Antimonious acid, Sb O_3 , is obtained by oxidating metallic antimony by nitric acid, or by roasting the sulphuret of antimony. It is the state of oxidation into which both oxide of antimony and antimonious acid pass, when ignited in open air. Antimonious acid is infusible and fixed, and is reduced to the metallic state with much greater difficulty than oxide of antimony. Fused with potash and separated afterwards from the alkali by an acid, it is obtained as a hydrate, containing 1 eq. of water, and having an acid reaction, $\text{SbO}_3 + \text{HO}$. It may also be viewed as a compound of antimonious acid with oxide of antimony.

When hydrated antimonious acid is digested in hydrochloric acid, a solution is obtained which is supposed to contain a corresponding chloride of antimony Sb Cl_3 . A corresponding sulphuret of antimony has also been formed.

Antimonic acid, Sb O_5 , is most easily prepared by the oxidation of oxide of antimony, by nitric acid, as arsenic acid is prepared from arsenious acid. The excess of nitric acid should then be expelled by a heat short of redness. Antimonic acid is a pale yellow powder, tasteless and insoluble in water. It displaces carbonic acid from the alkaline carbonates, and combines with the alkali. It is also soluble in a boiling solution of potash, from which acids precipitate hydrated antimonic acid as a white powder. In the hydrated state antimonic acid is soluble in hydrochloric acid, and also in solutions of the alkalies, without heat. *Antimoniate of soda* is uncrystallizable. *Antimoniate of potash* is prepared by deflagrating a mixture of 1 part of antimony, or of sulphuret of antimony, and 6 parts of nitre. The mass is first digested in cold water, which dissolves out nitrate and nitrite of potash, and leaves antimoniate of potash. When this residue is digested in boiling water, a binantimoniate of potash is left, and the neutral antimoniate dissolved out. The solution is feebly alkaline; when concentrated to the consistence of honey, it gives crystalline grains. All acids, even the carbonic, occasion a precipitate in this solution, which is the binantimoniate of potash, $\text{KO, Sb}_2\text{O}_{10}$. When a soluble salt of lime or of zinc is treated, at the boiling point, with the solution of the neutral antimoniate of potash, the antimoniate of lime or of zinc separates in a crystalline state; other salts of antimonic acid fall as an insoluble powder, when solutions of the different metallic oxides are precipitated by the neutral salt.

Many of the metallic antimoniates, particularly those of cobalt and copper, lose first their combined water when heated, and afterwards glow strongly when heated to redness. After that change, these antimoniates are not soluble either in acids or alkalies.

Sulphantimonic acid, Sb S_5 , is obtained when antimoniac acid or the following chloride of antimony is precipitated by sulphuretted hydrogen. It is of a much paler red colour than the other sulphurets of antimony, and constitutes the *golden sulphuret of antimony* of several pharmacopeias.

Pentachloride of antimony, Sb Cl_5 , is formed when metallic antimony in powder is gently heated in chlorine gas. The antimony burns with scintillations, and a colourless or slightly yellow coloured liquid distils over. This chloride condenses olefiant gas as readily as chlorine, and forms the Dutch liquid, the pentachloride being reduced at the same time to terchloride of antimony.

ORDER V.

METALS NOT INCLUDED IN THE FOREGOING CLASSES, OF WHICH THE OXIDES ARE NOT REDUCED BY HEAT ALONE.

URANIUM.

LANTANUM.

CERIUM.

TANTALUM.

URANIUM.

Eq. 2711.4 or 217.26 ; U.

This metal is derived from the mineral *pitchblende*, which consists principally of protoxide of uranium. The mineral is dissolved in aqua regia, and a stream of sulphuretted hydrogen passed through the liquor, by which copper, lead and arsenic are precipitated. The liquid is afterwards boiled, and the protoxide of iron peroxidised by means of nitric acid. An excess of ammonia is then added to the liquid, and the precipitate formed of oxides of uranium, iron, cobalt and zinc, is washed, then treated with a dilute solution of carbonate of ammonia, which leaves the peroxide of iron, and dissolves the other oxides. By boiling the yellow solution, the carbonate of ammonia is expelled, and the oxides precipitate. These are dried and ignited, by which protoxide of uranium is rendered insoluble in acids.

The other oxides are dissolved out of the ignited mass by hydrochloric acid, the protoxide of uranium remaining as a very fine, dark grey powder, which is received on a filter and washed well. Protoxide of uranium, obtained in this manner, may be dissolved, with the aid of heat, in concentrated sulphuric acid.

The peroxide of uranium is easily reduced by hydrogen. Arfwedson obtained the metal by passing hydrogen over the double chloride of uranium and potassium at a red heat, in the form of little regular octohedrons of a brilliant metallic lustre, and of a dark grey colour, almost black. The density of this metal is 9.00. It combines with oxygen in two proportions, forming a protoxide, UO , and peroxide U_2O_3 .

Protoxide of uranium, Uranous oxide, UO , 2811.4 or 225.26.—This oxide is obtained when an alkali is added to a solution of any of its salts, as a greenish grey hydrate, which soon becomes yellowish, and is finally converted into uranic oxide by the oxygen of the air. Carbonate of ammonia added in excess to a uranous salt, redissolves the precipitate and forms a green solution. The *uranous chloride*, UCl , forms a green syrupy solution which does not crystallize. The *uranous sulphate* yields, by evaporation, green prismatic crystals. This oxide is employed in painting upon porcelain, and yields a black of the greatest purity.*

Peroxide of uranium, Uranic oxide, U_2O_3 , 2911.4 or 233.26.—When an alkali is added to a salt of this oxide, a compound of uranic oxide and the alkali is precipitated and not the hydrated oxide itself; but the latter may be obtained by the oxidation of uranous oxide. The uranic hydrate is of a yellow colour, has an acid reaction upon litmus, and is decomposed by heat, allowing water and oxygen to escape, while uranous oxide remains. Uranic oxide forms insoluble compounds with

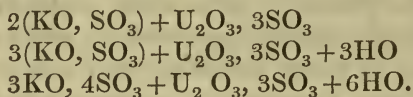
* The atomic weight of uranium, indicated by the specific heat of the metal, is only 677.8, or one-fourth of the number hitherto received, according to new researches of M. Regnault, (An. de Ch. et de Ph. t. 73, p. 71.) The oxide of uranium, at present considered as the protoxide, comes then to be U_4O . M. Regnault has added greatly to the value of specific heat, as an element in fixing atomic weights, by confirming Dulong's general results by new experiments, and also by removing several of the exceptions to the law, that all simple atoms have the same capacity for heat, noticed at page 124. The elements enumerated below have the same capacity for heat, in the following atomic proportions, by Regnault's experiments :

Bismuth .	1330	Cobalt .	369	Antimony .	806.4
Silver .	675.5	Selenium	494.6	Phosphorus .	196.1
Uranium .	677.8	Arsenic	470	Carbon .	152.9

the alkalies, alkaline earths and other metallic oxides. It is soluble in alkaline carbonates, particularly the bicarbonates, and the solution deposits, after a time, lemon yellow crystals of a double carbonate. The alkaline and earthy uranates assume, when ignited, a deep and very beautiful orange colour, which is most intense in the compounds with excess of base. This oxide is employed to colour glass of a delicate lemon-yellow tint.

Sesqui-chloride of uranium, $U_2 Cl_3$, is very soluble in water, alcohol and ether. It forms a double salt of remarkable beauty with chloride of potassium, which crystallizes from a syrupy solution, $3KCl + U_2 Cl_3 + 6HO$.

The *uranic sulphate* combines with sulphate of potash in three different proportions, forming the salts :



The proportion of the sulphuric acid and potash in the last salt is very extraordinary, but is the result of exact experiments, (Berzelius). The formula, however, is not to be supposed to express the proximate constitution of the salt.

The *uranic nitrate* is obtained by a slow evaporation in large tables, which like the other salts of this oxide are of a yellow colour. The nitrate is highly soluble both in water and alcohol. Uranic oxide is also said to form an *acid salt* with nitric acid, which is less soluble and more easily crystallized than the neutral salt.

The mineral *uranite* is a double phosphate of lime and uranium, of which the formula is $3Ca O, PO_5 + 2(U_2 O_3, PO_5) + 24HO$.

CERIUM.

Eq. 574.7 or 46.05 ; Ce.

This metal was named Cerium by Hisinger and Berzelius, from Ceres. Although not an abundant element, it is found in a considerable number of minerals all from Sweden and Greenland. The mineral *cerite* is a cerous silicate, containing 68.6 per cent of cerous oxide, with small quantities of lime and peroxide of iron. This mineral is boiled in aqua regia, by which the silica is separated, and the other oxides dissolved. The iron is precipitated by benzoate of ammonia, and then

ammonia added to the liquid, which throws down a mixture of cerous and ceric oxides. The oxides of cerium are reduced with difficulty, but by decomposing the cerous chloride by potassium, the metal was obtained by Mosander as a pulverulent mass of a dark chocolate brown, which gave a grey metallic trace under the burnisher. It oxidates quickly in water, disengaging hydrogen gas, particularly when the water is a little heated.

Protoxide of cerium, Cerous oxide, Ce O , is procured by calcining the mixed oxides of cerium, obtained as already described, by precipitating the solution of cerite in an acid by ammonia, till chlorine is no longer disengaged, as perceived by its odour. The salt that remains, when dissolved in water and precipitated by an alkali, gives the hydrate of cerous oxide, which soon becomes yellow in the air. The cerous salts are generally colourless, although some of them have an amethystine colour, like the salts of manganese. Their taste is sweet and afterwards astringent and they greatly resemble the salts of yttria. From these they may be distinguished by forming a salt with sulphate of potash of small solubility. They are precipitated white by the yellow prussiate of potash, not affected by sulphuretted hydrogen, and precipitated by an alkaline sulphuret with disengagement of sulphuretted hydrogen gas.

Peroxiide of cerium, Ceric oxide, $\text{Ce}_2 \text{O}_3$, is obtained by calcining the cerous nitrate or carbonate. The ignited oxide is brick red and pulverulent, easily soluble in acids, from which it is thrown down by an alkali as a mucilaginous matter, of a clear yellow colour, which is the hydrated oxide. This hydrate is not soluble in caustic alkalies, but alkaline carbonates dissolve a small quantity of it and become yellow. An intermediate compound, the *ceroso-ceric oxide*, is obtained when ceric oxide is exposed to hydrogen at a red heat. It is a lemon yellow powder, which passes into ceric oxide by combustion in air. The salts of ceric oxide are distinguished from those of cerous oxide by their yellow and sometimes orange colour, by their taste which is sweetish-sour and strongly astringent. They are decomposed when boiled with hydrochloric acid, and converted into cerous salts with evolution of chlorine.

LANTANUM.

The oxide of this new metal was lately discovered by Mosander to exist in the cerite of Bastnas, forming indeed two

fifths of what is extracted from that mineral, by the ordinary process, as oxide of cerium. This throws considerable uncertainty over our knowledge of cerium, as the observations of chemists have not been made upon a pure substance. The new element alters but little the properties of cerium, and lies, therefore, as if concealed in it; it was that fact which induced M. Mosander to apply the name *lantanium* to the new metal. The oxide of lantanum is not reduced by potassium, but this metal separates from the chloride of lantanum a grey metallic powder, which undergoes oxidation in water, with disengagement of hydrogen gas, changing into a white hydrate.

Oxide of lantanum.—It is prepared by calcining the nitrate of cerium as it is mixed with nitrate of lantanum. The oxide of cerium loses its solubility in very dilute acids, while the oxide of lantanum may be taken up by nitric acid diluted with 100 parts of water. The ignited oxide of lantanum has a brick red colour, which does not appear to be due to oxide of cerium. It changes in hot water into a white hydrate, which makes red litmus paper blue. This oxide is so powerful a base, that when digested in a solution of sal ammoniac, it dissolves by degrees, expelling the ammonia. The atomic weight of lantanum is smaller than that assigned to cerium or rather to the mixture of the two metals, but has not been accurately determined.

Sulphuret of lantanum is produced on heating the oxide strongly in the vapour of the sulphuret of carbon. It is pale yellow, decomposes water with disengagement of sulphuretted hydrogen, and becomes the hydrated oxide.

The salts of lantanum have an astringent taste without any mixture of sweetness. Their crystals have generally a rose tint; sulphate of potash produces a precipitate in them, only when they are mixed with salts of cerium.

TANTALUM.

Syn. COLUMBIUM. *Eq.* 2307.4 or 184.9; Ta.

This metal appears to have been first observed in 1801, by Mr. Hatchett, in a black mineral belonging to the British Museum, and supposed to have come from Massachusetts in North America, and was named columbium on that account. M. Ekeberg found a new metal in 1802, which he called tantalum, in two Swedish minerals, then new, and named by him

tantalite and yttrotantalite. Their metal was fully studied by Berzelius; and columbium, which had been imperfectly examined by Hatchett, was found by Dr. Wollaston, in 1809, to be the same metal. Tantalum has since been observed in two or three other minerals, but all of them among the rarest species.

Tantalum is not reduced by carbon, but Berzelius obtained it by decomposing the double fluoride of silicon and potassium by potassium. It was a black powder, which could be washed and dried, and assumed an iron grey metallic lustre under the burnisher. It took fire in air below a red heat and burned with much vivacity, yielding tantalic acid. No acid has a sensible action upon tantalum except hydrofluoric acid. Tantalum combines with oxygen in two proportions, forming tantalic oxide, Ta O_2 , and tantalic acid, Ta O_3 .

Tantalie oxide, Ta O_2 , 2507.4 or 200.9.—This oxide is obtained on exposing tantalic acid in a charcoal crucible to the heat of a wind furnace, for an hour and a half. With the exception of the external film immediately in contact with the charcoal, which is metallic tantalum, the mass of acid is converted into tantalic oxide. This oxide is of a dark grey colour, its particles are so hard as to scratch glass; it is soluble in no acid, not even in aqua regia or hydrofluoric mixed with nitric acid. The name tantalum was applied to the metal by Ekeberg, on account of this insolubility of its oxide in acids, in allusion to the fable of Tantalus. Heated to low redness in air, it burns slowly, and is converted, although not entirely, into tantalic acid.

Tantalie acid, Ta O_3 , 2607.4 or 208.9.—It is in the state of tantalic acid that tantalum exists in most of its minerals, combined with the oxides of iron and manganese in tantalite, or with yttria in yttrotantalite. The acid may be obtained by fusing the mineral with carbonate of potash, and decomposing the tantalate of potash formed, by an acid, and also by fusion with bisulphate of potash (Berzelius, *Traité*, I, 392). It presents itself as a white powder, which reddens litmus paper; when distilled in a retort, it parts with its water, which amounts to $11\frac{1}{2}$ per cent, $\text{Ta O}_3 + 3\text{HO}$, and loses the latter property. The density of the ignited acid is 6.5, in this state it is attacked by alkalis only. Tantalie acid dissolves by fusion in bisulphate of potash, and when hydrated in binoxalate of potash by the

humid way. It is dissolved in small quantity by concentrated sulphuric acid, but precipitated from that solution by water.

Sulphotantalic acid, TaS_3 , is prepared with most advantage by exposing tantalic acid to a bright red heat in a porcelain tube, and passing bisulphuret of carbon over it. It forms a grey pulverulent matter, having much the appearance of plumbago. It is a good conductor of electricity.

Chloride of tantalum, $TaCl_3$, obtained on heating tantalum in pure chlorine gas, is, in the state of vapour, a yellow gas resembling chlorine, which condenses into a white floury powder, having a shade of yellow, and in no way crystalline.

Tantalic acid dissolves in alkalies and forms salts, but they are not crystallizable and are decomposed by all other acids even by carbonic acid.

ORDER VIII.

METALS OF WHICH THE OXIDES ARE REDUCED TO THE METALLIC STATE BY HEAT (NOBLE METALS.)

SECTION I.

MERCURY.

Eq. 1265.8 or 101.43 ; Hg (*hydrargyrum*.)

Mercury or quicksilver, as it is named from its fluidity, has been known from all antiquity. The most valuable European mines of this metal are those of Idria in Illyria, and Almaden in Spain. It is found, to a small extent, in the metallic state. Its principal ore is a sulphuret, native cinnabar, from which the metal is obtained by distillation with lime or iron. The quicksilver of commerce is in general a highly pure substance. When contaminated with other metals, its fluidity is remarkably impaired. Mercury may be purified by distilling it from half its weight of iron turnings, or by digesting the metal with a small quantity of nitric acid, or with a solution of chloride of mercury, which rids it of the metals more oxidable than itself.

Mercury is liquid at the usual temperature, its colour is white with a shade of blue when compared with silver, and it has a

high metallic lustre. When pure, its surface does not tarnish in air. At 39 or 40 degrees below zero, mercury becomes solid; it crystallizes in regular octohedrons. According to M. Kupffer, the density of mercury at 39.2° is 13.5886; at 62.6°, 13.5569. and at 78.8°, 13.535. In the solid state, its density is about 14.0. At 662° it boils, forming a colourless vapour, of which the density was observed to be 6976, by Dumas; the theoretical density is 6978. Mercury emits a sensible vapour between 68° and 80°, but not under 40°. When heated near its boiling point, mercury absorbs oxygen from the air, and forms crystalline scales of the red oxide. It is not affected by boiling hydrochloric or diluted sulphuric acid, but is readily dissolved by diluted nitric acid. This metal never dissolves in hydrated acids, by substitution for hydrogen. Mercury combines with oxygen in two proportions, forming the black oxide, which is generally considered a suboxide, Hg_2O , and the red oxide, composed of single equivalents, Hg O , both of which are bases. The equivalent of mercury is then assumed to be 1265.8; but whether it should be this number or a multiple of it by two, we have no certain means of deciding, while in ignorance of any isomorphous relation of mercury with the magnesian metals.

MERCUROUS COMPOUNDS.

Suboxide of mercury (black oxide), Mercurous oxide, Hg_2O , 2631.6 or 210.86.—This oxide is obtained by the action of a cold solution of potash, used in excess, upon calomel. They should be mixed briskly together in a mortar, in order that the decomposition be as rapid as possible, and the oxide be allowed to dry spontaneously in a dark place. Mr. Donovan finds these precautions necessary, from the disposition which this oxide possesses, to resolve itself into metallic mercury and the higher oxide. The decomposition of mercurous oxide is promoted by elevation of temperature, and by exposure to light. The mercurous oxide is a black powder, of which the density is 10.69 (Herapath); it unites with acids and forms a class of salts. It is precipitated as the black oxide by lime-water and the pure alkalies, and by alkaline carbonates as a white carbonate, which soon becomes black from decomposition. Its soluble salts are all partially decomposed by pure water, which combines with a portion of their acid, and throws down a subsalt containing an excess of oxide. They are precipitated black by sulphuretted

hydrogen. The salts of the same oxide are decomposed by hydrochloric acid and soluble chlorides, with precipitation of calomel as a white powder, a property by which they are distinguished from the salts of the red oxide of mercury.

The salts of this, and also of the red oxide, are reduced to the metallic state by copper and more oxidable metals, and by the proto compounds of tin. The precipitated mercury often presents itself as a grey powder, in which metallic globules are not perceived, and remains in this condition while humid. Mercury in this divided state possesses the medicinal qualities of the milder mercurials, and has often been mistaken for black oxide. To obtain *precipitated mercury*, equal weights of crystallized protochloride of tin (salt of tin) and corrosive sublimate may be dissolved, the first in diluted hydrochloric acid and the second in hot water, and the solutions mixed with stirring. The salt of tin assumes the whole chlorine of the corrosive sublimate, becoming bichloride of tin, which remains in solution, while the mercury is liberated, and forms so fine a precipitate, that it requires several hours to subside. It may be washed by affusion of hot water and subsidence, and slightly drained on a filter, but not allowed to dry. There can be no doubt that it is in this divided state, and not as the black oxide, that mercury is obtained by trituration with fat, turpentine, syrup, saliva, &c., in many pharmaceutical preparations.

Subsulphuret of mercury, Hg_2S , is obtained by the action of sulphuretted hydrogen on a solution of the mercurous nitrate or upon calomel, as a black precipitate. This sulphuret is decomposed by a gentle heat, and resolved into globules of mercury and the higher sulphuret.

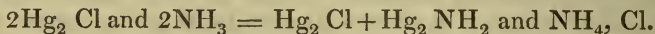
Subchloride of mercury, Calomel, Hg_2Cl , 2974.3 or 238.33. —A variety of processes are given by pharmacians for the preparation of this remarkable substance. It may be obtained in the humid way, by digesting $1\frac{1}{8}$ parts of mercury, with 1 part of pure nitric acid, of density from 1.2 to 1.25, till the metal ceases to be dissolved, and the liquid has begun to assume a yellow tint. A solution is also prepared of 1 part of chloride of sodium in 32 parts of distilled water, to which a certain quantity of hydrochloric acid is added, and this when heated to near the boiling point, is mixed with the mercurial salt. The mercury acquires the chlorine of the common salt, and the subchloride of mercury formed precipitates as a white powder, while

the nitric acid and oxygen are resigned by the mercury to the sodium, which becomes nitrate of soda: Na Cl and $\text{Hg}_2 \text{O}$, $\text{NO}_5 = \text{Hg}_2 \text{Cl}$ and NaO , NO_5 . The excess of acid in this process is intended to prevent the precipitation of any subnitrate of mercury, which the dilution of the nitrate of mercury, on mixing the solutions, might occasion the formation of. Calomel is also obtained by rubbing together, in a mortar, 4 parts of chloride of mercury (corrosive sublimate) with 3 parts of running mercury. The mixture is afterwards introduced into a glass balloon, and sublimed by a heat gradually increased. Here the chloride of mercury combines with mercury, and the subchloride is produced. The same result is obtained by mixing the sulphate of red oxide of mercury, with as much mercury as it already contains, and about one third of its weight of chloride of sodium, and subliming the mixture. The vapour of the subchloride of mercury, in these sublimations, is advantageously condensed by conducting it into a vessel containing hot water; the vapour of the water then condenses the salt in an extremely fine and beautifully white powder. The product of this operation is recommended by its purity, as well as its minute division, for chloride of mercury, by which the subchloride is accompanied, is dissolved by the water. It appears that whenever the subchloride is sublimed, a small portion of it is resolved into mercury and the chloride. To prepare the calomel for medical use, as it is usually condensed in a solid cake, it must, therefore, be reduced to a fine powder, and also be washed with hot water to remove the soluble chloride.

Subchloride of mercury is obtained by sublimation in four-sided prisms, terminated by summits of four faces. When the solid cake is finely pounded, the salt acquires a yellow tinge. The density of this salt in the solid condition is 6.5; in the state of vapour 8200, one volume of which contains one volume of the vapour of mercury and half a volume of chlorine. This salt is so highly insoluble in water, that when the mercurous nitrate is added to hydrochloric acid diluted with 250,000 times its weight of water, a sensible precipitate of subchloride of mercury appears. When boiled for a long time in hydrochloric acid, this salt is resolved into chloride of mercury which dissolves, and mercury which is reduced.

Action of ammonia on subchloride of mercury.—The dry subchloride was found by Rose to absorb half an equivalent of am-

monia, and to become black. Exposed to air the compound loses its ammonia, and the subchloride of mercury recovers its white colour. This ammoniacal compound is $2\text{Hg}_2\text{Cl} + \text{NH}_3$. When calomel is digested in solution of ammonia, it becomes black, and was found by Dr. Kane to be converted into a double *subamide and subchloride of mercury*, a portion of sal ammoniac being dissolved by the water at the same time:



This compound is not altered by boiling water; when quite dry, it is of a grey colour.

Subbromide of mercury, Hg_2Br , is a white insoluble powder, resembling in all respects the subchloride, and formed in similar circumstances. A boiling solution of chloride of strontium was found by Lœwig to dissolve 3 equivalents of calomel, of which 1 eq. precipitated, during the cooling of the solution. When the filtered solution was evaporated, it deposited a salt in small crystals, $\text{Sr Br} + 2\text{Hg}_2\text{Br}$. These crystals were decomposed by pure water, and resolved into the insoluble subbromide Hg_2Br , and a double salt which dissolved easily and crystallized by evaporation, $\text{Sr Br} + \text{Hg}_2\text{Br}$.

Subiodide of mercury, Hg_2I , is obtained by precipitation as a green powder, which is red when heated. It is also formed by triturating mercury and iodine together in a mortar, with a few drops of alcohol, in the proportion of 2 eq. of the former to 1 eq. of the latter. Another iodide of mercury was obtained by Boullay, by precipitating nitrate of suboxide of mercury with a solution of iodide of potassium, to which half an equivalent of iodine had been previously added. It is a yellow powder, which may be washed with alcohol; from its composition it appears to be a compound of single equivalents of neutral iodide and subiodide of mercury, $\text{Hg I} + \text{Hg}_2\text{I}$.

No *subcyanide of mercury* exists, and it is doubtful whether a *subfluoride*, corresponding with the suboxide has been formed.

Carbonate of black oxide of mercury, $\text{Hg O}_2, \text{CO}_2$, precipitates as a white powder, when an alkaline carbonate is added to the nitrate of the same oxide. The precipitate becomes grey when the liquid containing it is boiled, and carbonic acid escapes. This carbonate is soluble both in carbonic acid water, and in an excess of alkaline carbonate.

Sulphate of black oxide of mercury, Mercurous sulphate, HgO , SO_3 ; 3132.8 or 251.04.—It is obtained by digesting 1 part of mercury in $1\frac{1}{2}$ parts of sulphuric acid, avoiding a high temperature, and interrupting the process as soon as all the mercury is converted into a white salt. It is also precipitated when sulphuric acid is added to a solution of the nitrate of the same oxide. The salt may be washed with a little cold water. It crystallizes in prisms, and requires 500 times its weight of cold and 300 of hot water to dissolve it. With water of ammonia this salt gives a dark grey powder, containing ammonia or its elements.

Nitrates of black oxide of mercury, Mercurous nitrates.—The *neutral nitrate* is obtained, when mercury is dissolved in an excess of cold nitric acid, and crystallizes readily in transparent rhombs. It is soluble with heat in a small quantity of water, but is decomposed by a large quantity of water, and an insoluble subsalt formed, unless nitric acid be added to the water. The formula of this salt is Hg_2O , $\text{NO}_5 + 2\text{HO}$. A *subnitrate* is formed when the black oxide is dissolved in a solution of the preceding salt, or when an excess of mercury is digested in diluted nitric acid at the usual temperature. It crystallizes readily in white and opaque rhombic prisms, which contain, according to both G. Mitscherlich and Kane, 2NO_5 , $3\text{Hg}_2\text{O}$ and 3HO . This salt was observed by the former chemist to be dimorphous. When dissolved by dilute nitric acid, it gives the neutral salt. The subnitrate is soluble in a little water, but when treated with a large quantity, it leaves undissolved, like the neutral nitrate, a white powder, which as long as the supernatant liquid is acid retains its colour, but if it be washed with water becomes yellow. The *yellow subnitrate of mercury* was found to contain NO_5 , $2\text{Hg}_2\text{O}$ and HO (Kane). When very dilute ammonia is added to the preceding soluble nitrates, without neutralising the whole acid, a velvety black precipitate falls, known as *Hahnemann's soluble mercury*. This salt contains, according to the analysis of G. Mitscherlich, NO_5 , $3\text{Hg}_2\text{O}$ and NH_3 . But when pains were taken to avoid decomposition of the salt in washing it, its composition was found by Dr. Kane to be NO_5 , $2\text{Hg}_2\text{O}$ and NH_3 .

Acetate of black oxide of mercury, Hg_2O , $\text{C}_4\text{H}_3\text{O}_3$, falls, when acetic acid or an acetate is added to the nitrate, in crystalline scales of a pearly lustre. It is anhydrous, and sparingly soluble in water.

MERCURIC COMPOUNDS.

Oxide of mercury (red oxide), Mercuric oxide, Hg O, 1365.8 or 109.43.—This compound is formed by the oxidation of mercury at a high temperature, as has already been described, or by heating the nitrate of mercury till all the nitric acid is expelled, and the mass, calcined almost to redness, no longer emits vapours of nitric oxide. As prepared by the last process, oxide of mercury forms a brilliant orange-red powder, crystallized in plates, and having the density 11.074. It is very dark red at a high temperature, but becomes paler as it cools. When reduced to a fine powder it becomes yellow, like litharge, without any shade of red. It was found by Mr. Donovan to be soluble to a small extent in water. If contaminated with nitric acid, it gives off nitrous fumes when heated in a glass tube, and a yellow sublimate of subnitrate also appears. This oxide is known in pharmacy as *red precipitate*. The same substance is obtained by precipitation, when a solution of corrosive sublimate is mixed with an excess of caustic potash, as a dense powder of a lemon-yellow colour. It is necessary to use the potash in excess, otherwise a dark brown oxichloride is formed. The precipitated oxide parts with a little moisture, when gently heated, but does not change in appearance. At a red heat, the oxide of mercury is entirely volatilised in the form of oxygen and metallic mercury.

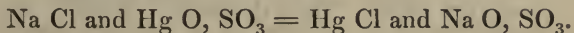
When water of ammonia is digested for several days upon precipitated oxide of mercury, the latter is converted into a yellowish-white powder, which Dr. Kane considers as $\text{Hg, NH}_2 + 2\text{Hg O} + 3\text{HO}$, or a hydrated compound of amide and oxide of mercury.

Sulphuret of mercury, Cinnabar, Hg S, 1467 or 117.55.—This is the common ore of mercury, and sometimes occurs crystallized forming a beautiful vermilion. It is prepared artificially, by fusing one part of sulphur in a crucible, and adding to it by degrees six or seven parts of mercury, stirring it after each addition, and covering it to preserve it from contact of air, when it inflames from the heat evolved in the combination. The product is exposed to a sand bath heat, to expel the sulphur uncombined with mercury, and afterwards sublimed in a glass matrass by a red heat. A brilliant red mass of a crystalline structure is thus obtained, which when reduced to fine

powder forms the lively red pigment, vermilion. This sulphuret is black before sublimation. It is precipitated black also when sulphuretted hydrogen is sent through a solution of corrosive sublimate; but is of the same composition in both states. The sulphuret of mercury, however, may be obtained of a red colour without sublimation, or in the humid way, by several methods.

Liebig recommends for this purpose to moisten the preparation called white precipitate, recently prepared, with the sulphuret of ammonium, and allow them to digest together. The black sulphuret is instantly produced, which in a few minutes passes into a fine red cinnabar, the colour of which is improved by digesting it at a gentle heat in a strong solution of hydrate of potash. The sulphuret of ammonium used in this experiment is prepared by dissolving sulphur in hydrosulphuret of ammonia to saturation. Cinnabar is not attacked by sulphuric, nitric or hydrochloric acid, nor by solutions of the alkalies, but it is dissolved by aqua regia.

Chloride of mercury, Corrosive sublimate, 1708.5 or 136.9.—This salt may be formed by dissolving red oxide of mercury in hydrochloric acid, or by adding hydrochloric acid to any soluble salt of that oxide, but it is generally prepared in a different manner. Four parts of mercury are added to five parts of sulphuric acid, and the mixture boiled till it is converted into a dry saline mass. The mercuric sulphate thus obtained is mixed with an equal weight of common salt, and heated strongly in a retort by a sand bath; chloride of mercury sublimes and condenses in the upper part and neck of the retort, while sulphate of soda remains behind with the excess of chloride of sodium. The mercury and sodium have exchanged places in the salts:



Mercury, when heated in a stream of chlorine gas, burns with a pale flame, and is converted into a white sublimate of chloride. The salt has been prepared on a large scale in this manner, which was suggested as a manufacturing process by Dr. A. T. Thomson.

The sublimed chloride of mercury forms a crystalline mass, of which the density is 6.5; it fuses at 509°, and boils about 563°. The vapour of chloride of mercury is colourless, its density 9420, 1 volume of it containing 1 volume of mercury vapour

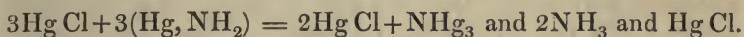
and 1 volume of chlorine gas. This salt is soluble in 16 parts of cold and in 3 parts of boiling water, in $2\frac{1}{3}$ parts of cold and in $1\frac{1}{2}$ part of boiling alcohol, and in 3 parts of cold ether. It is not decomposed by sulphuric or nitric acid; is largely dissolved by the latter and also by hydrochloric acid. It is obtained by sublimation and from solution, in two different crystalline forms. The solutions of chloride of mercury exposed to the direct rays of the sun evolve oxygen, while hydrochloric acid is dissolved and subchloride of mercury precipitates. The decomposition of this salt, by the action of light, is greatly more rapid when the solution contains organic matter. The poisonous action of chloride of mercury, which is scarcely inferior to that of arsenious acid, is best counteracted by liquid albumen, with which chloride of mercury forms an insoluble and inert compound.

The solution of chloride of mercury affords a yellow or brown precipitate with the hydrates of potash and soda, and with lime water; a black precipitate with sulphuretted hydrogen, and a fine scarlet precipitate with iodide of potassium. Mercury is thrown down from that solution by metallic copper. A drop of the solution does not tarnish polished gold, but if the moistened surface be touched by zinc or iron, mercury is immediately precipitated, and produces a blue stain upon the surface of the gold, while the common metal dissolves.

Chloride of mercury and ammonia.—When chloride of mercury is gently heated in a stream of ammoniacal gas, the latter is absorbed, and the compound fuses from heat evolved in the combination. The product was found by Rose to contain half an equivalent of chlorine, $2\text{Hg Cl} + \text{NH}_3$. This compound boils at 590° and may be distilled without loss of ammonia; it is decomposed by water. When the double chloride of mercury and ammonium, called sal alembroth, is precipitated by potash in the cold, a white powder is obtained, which was first distinguished by Wöhler from the compound next described; its composition may be expressed, from the analysis of Dr. Kane, by $\text{Hg Cl} + \text{NH}_3$. The same compound is also formed when ammonia is added to a solution of sal ammoniac, and chloride of mercury dropt into the liquid, brought to the boiling point, so long as the precipitate which is produced is redissolved. The compound appears on the cooling of the solution, in small crystals, which are garnet dodekahedrons (Mitscherlich). The

crystalline form of this compound, therefore, belongs to the regular system, like that of sal ammoniac.

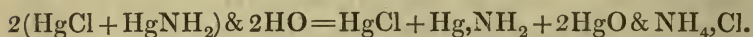
The compound known as *white precipitate*, is formed when ammonia is added to a solution of chloride of mercury. When first produced, it is bulky and milk white; it is decomposed by hot water or by much washing with cold water, and acquires a yellow tinge. Dr. Kane has demonstrated that white precipitate is free from oxygen, and contains nothing but the elements of a double chloride and amide of mercury, and represents it by the formula, $\text{Hg Cl} + \text{Hg, NH}_2$. White precipitate is distinguished from calomel by solution of ammonia, which does not alter the former, but blackens the latter; it is readily dissolved by acids. Mitscherlich has observed that when white precipitate is gradually heated by a metal bath, and the heat continued for a long time, three atoms of it lose two atoms of ammonia and one atom of chloride of mercury, while a red matter remains in crystalline scales, having much the appearance of red oxide of mercury produced by the oxidation of the metal in air, which contains two atoms of chloride of mercury united with a compound of one atom of nitrogen and three atoms of mercury, $2\text{Hg Cl} + \text{NHg}_3$. He concludes, that the atom of white precipitate should be multiplied by three, its decomposition by the heat of the metal bath would then be represented thus :



The red compound is itself decomposed by a temperature above 680° , and resolved into chloride of mercury, mercury and nitrogen. It is insoluble in water, and is not altered in boiling solutions of the alkalies. It may be boiled without change in diluted or concentrated nitric acid, and in pretty concentrated sulphuric acid, but it is decomposed and dissolved when boiled in the most concentrated sulphuric acid or in hydrochloric acid; no gas is evolved, but chloride of mercury and ammonia are found in the acid solution. The compound NHg_3 is not isolated, by passing ammonia over the heated red compound. Mercury conducts itself in these compounds in the same way as potassium with ammonia; the olive coloured substance produced by the action of dry ammonia upon potassium being the amide of potassium, $3(\text{K, NH}_2)$, and the plumbago looking substance left on heating

the amide of potassium, when ammonia escapes, a compound of nitrogen and potassium, NK_3 .*

When white precipitate is boiled in water, it is changed into a heavy *canary yellow powder*, which Dr. Kane has shewn to be a compound of the double chloride and amide of mercury with oxide of mercury, $Hg\ Cl + Hg, NH_2 + 2HgO$. Two atoms of water are decomposed in its formation, the two atoms of oxygen which are found in the yellow compound, while the two atoms of hydrogen, added to an atom of chlorine and an atom of amidogen, form an atom of hydrochlorate of ammonia which is found in solution :



Solutions of potash and soda convert white precipitate into the same yellow substance, while a metallic chloride is formed and ammonia evolved (Kane).

Oxichloride of mercury.—When a solution of corrosive sublimate is precipitated by potash or soda, mercuric oxide goes down in combination with a portion of chloride, as a brown precipitate, unless a considerable excess of alkali be employed. The same oxichloride is produced by an alkaline carbonate, but a double carbonate is then also formed. Chloride of mercury is not immediately precipitated by the bicarbonates of potash and soda, and, hence, that salt may be employed to detect the presence of a neutral alkaline carbonate in these bicarbonates. This oxichloride may also be formed by passing chlorine through a mixture of water and oxide of mercury. It may be obtained crystalline and of a very dark colour, almost black, by mixing corrosive sublimate with chloride of lime, and boiling the liquid, or by treating a solution of corrosive sublimate with bicarbonate of potash, and allowing the solution to stand in an open vessel, when carbonic acid gradually escapes, and the compound $HgCl + 4Hg\ O$ is deposited. This oxichloride is decomposed by a moderate heat, chloride of mercury sublimes and the red oxide is left.

Chloride and sulphuret of mercury, $Hg\ Cl + 2Hg\ S$.—When sulphuretted hydrogen gas is passed through a solution of chloride of mercury, the precipitate which first appears, and does not subside readily, is white; it has been shown by Rose to be a

* Mitscherlich in Poggendorff's Annalen, vol. 39, p. 409.

compound of chloride and sulphuret of mercury. This substance is changed entirely into sulphuret of mercury, when left in water containing sulphuretted hydrogen. On the other hand, precipitated sulphuret of mercury digested in a solution of chloride of mercury, takes down that salt and forms the compound in question. Sulphuret of mercury combines likewise with the bromide, iodide, fluoride and nitrate of mercury, and always in the proportion of two atoms of the sulphuret to one atom of the other salt.

Double salts of chloride of mercury.—Chloride of mercury was found by M. Bonsdorff to combine with *chloride of potassium* in three different proportions, forming a series of salts in which the chloride of potassium remains as one equivalent, while the chloride of mercury goes on increasing. They are, $\text{KCl} + \text{Hg Cl} + \text{HO}$, which crystallizes in large transparent rhomboidal prisms; $\text{KCl} + 2\text{Hg Cl} + 2\text{HO}$ crystallizing in fine needle-like amianthus; and $\text{KCl} + 4\text{Hg Cl} + 4\text{HO}$, which crystallizes also in fine needles. *Chloride of sodium* forms only one compound, $\text{Na Cl} + 2\text{Hg Cl} + 4\text{HO}$ which crystallizes in fine regular hexahedral prisms. One of the double salts of *chloride of ammonium* has long been known as *sal alembroth*. It crystallizes in flattened rhomboidal prisms, $\text{NH}_4 \text{Cl} + \text{Hg Cl} + \text{HO}$, and is isomorphous with the corresponding potash salt. It loses the water it contains in dry air, without change of form. Dr. Kane has also obtained $\text{NH}_4 \text{Cl} + 2\text{Hg Cl}$, and the same with an atom of water, $\text{NH}_4 \text{Cl} + 2\text{Hg Cl} + \text{HO}$, the first in a rhomboidal form, and the second in long silky needles. All these double chlorides are obtained by dissolving their constituent salts together in the proper proportions. *Chlorides of barium and strontium* form compounds in good crystals with *chloride of mercury*, $\text{Ba Cl} + 2\text{Hg Cl} + 4\text{HO}$, and $\text{Sr Cl} + 2\text{Hg Cl} + 2\text{HO}$. *Chloride of calcium* combines in two proportions with the mercurial chloride. When chloride of mercury is dissolved to saturation in chloride of calcium, tetrahedral crystals separate from the solution, which are pretty persistent in air, $\text{Ca Cl} + 5\text{Hg Cl} + 8\text{HO}$. After the deposition of these crystals, the liquid affords, when evaporated by a gentle heat, a second crop of large prismatic crystals, $\text{Ca Cl} + 2\text{Hg Cl} + 6\text{HO}$, which are very deliquescent. *Chloride of magnesium* also forms two salts, $\text{Mg Cl} + 3\text{Hg Cl} + \text{HO}$, and $\text{Mg Cl} + \text{Hg Cl} + 6\text{HO}$, both deliquescent. *Chloride of nickel* gives

two compounds, of which, one crystallises in tetrahedrons, like the chloride of calcium salt. *Chloride of manganese* forms a compound in good crystals, $\text{Mn Cl} + \text{Hg Cl} + 4\text{HO}$. *Chlorides of iron and zinc* form similar isomorphous salts, $\text{Fe Cl} + \text{Hg Cl} + \text{HO}$, and $\text{Zn Cl} + \text{Hg Cl} + \text{HO}$. The double chlorides of zinc and of manganese are remarkable in one respect, that chloride of mercury dissolved by them in excess, crystallizes by evaporation in fine large crystals, such as cannot be obtained in any other way. *Chlorides of cobalt, nickel and copper* form similar crystallizable salts; but chloride of lead, on the contrary, does not appear to form a double salt with chloride of mercury (Bonsdorff).

Bromide of mercury, Hg Br , 2244.1 or 179.82.—This salt is obtained by treating mercury with water and bromine. It is colourless, soluble in water and alcohol, and when heated, fuses and sublimes, exhibiting a great analogy to chloride of mercury in its properties. Its density in the state of vapour is 12,370. Bromide of mercury forms a similar compound with sulphuret of mercury $\text{Hg Br} + 2\text{Hg S}$, which is yellowish. It was also combined, by Bonsdorff, with a variety of alkaline and earthy bromides. Bromide of mercury combines with half an equivalent of ammonia, in the dry way, and also gives a white precipitate, with solution of ammonia, analogous to that derived from chloride of mercury.

Iodide of mercury, Hg I , 2845.3 or 228.—It falls as a precipitate of a fine scarlet colour, when iodide of potassium is added to a solution of chloride of mercury. It may also be obtained by triturating its constituents together, in the proper proportion, with a few drops of alcohol. To procure it in crystals, M. Mitscherlich dissolves iodide of mercury to saturation, in a hot concentrated solution of the iodide of potassium and mercury, and allows the solution to cool gradually. When heated moderately, iodide of mercury becomes yellow; at a higher temperature it fuses and sublimes, condensing in rhomboidal plates of a fine yellow colour. The forms of the red and yellow crystals are totally different, so that the change of colour is due to the dimorphism of iodide of mercury. The yellow crystals generally return gradually into the red state, when cold, and this change may be determined at once by scratching the surface of a crystal, or by crushing it. The density of iodide of mercury in the state of vapour, is 15,680; it is the heaviest of

gaseous bodies. Iodide of mercury is slightly soluble in water, but requires more than 6000 times its weight of water to dissolve it. It is much more soluble in alcohol and in acids, particularly with the assistance of heat. Iodide of mercury is very soluble in iodide of potassium; it is also dissolved by a hot solution of chloride of mercury.

When treated with sulphuretted hydrogen water, iodide of mercury forms the compound $\text{Hg I} + 2\text{Hg S}$, which is yellow. Iodide of mercury absorbs a whole equivalent of dry ammoniacal gas, $\text{Hg I} + \text{NH}_3$. The compound is white, but loses ammonia in the air and becomes red. Iodide of mercury unites with other iodides, and forms a class of salts as extensive as the compounds of chloride of mercury. They have been studied by M. P. Boullay.* Iodide of mercury also combines with chlorides; it is dissolved by a hot solution of chloride of mercury, and two compounds have been obtained on the cooling of the solution, a yellow powder, $\text{Hg I} + \text{Hg Cl}$, and white dendritic crystals, $\text{Hg I} + 2\text{Hg Cl}$.

Cyanide of mercury, Hg Cy , 1595.7 or 127.87.—This salt is most easily obtained by saturating hydrocyanic acid with red oxide of mercury. To prepare the hydrocyanic acid required, the process of Winkler may be followed. Fifteen parts of ferrocyanide of potassium are distilled with 13 parts of oil of vitriol diluted with 100 parts of water, and the distillation continued by a moderate heat nearly to dryness. The vapour should be made to pass through a Liebig's condensing tube, and be afterwards received in a flask containing 30 parts of water. A portion of the condensed hydrocyanic acid is put aside, and the remainder mixed with 16 parts of oxide of mercury in fine powder, and well agitated till the odour of hydrocyanic acid is no longer perceptible. The solution is drawn off from the undissolved oxide of mercury, and the reserved portion of hydrocyanic acid mixed with it. The last addition is necessary to saturate a portion of oxide of mercury, which cyanide of mercury dissolves in excess. This operation yields 12 parts of the salt in question. Cyanide of mercury crystallizes in square prisms, which are anhydrous, and resembles chloride of mercury in its solubility and poisonous qualities. The red oxide of mercury, even when dry, absorbs hydrocyanic

* An. de Chim. et de Phys., t. 34, p. 337.

acid, with the formation of water and evolution of heat. The affinity of mercury for cyanogen appears to be particularly intense; oxide of mercury decomposing all the cyanides, even cyanide of potassium and liberating potash. Cyanide of mercury is consequently not precipitated by potash. Nor is it decomposed by any acid, with the exception of hydrochloric, hydriodic and sulphuretted hydrogen. By a heat approaching to redness, cyanide of mercury is decomposed, and resolved into mercury and cyanogen gas. When hydrocyanic acid is digested upon mercurous oxide, the mercuric cyanide dissolves, and metallic mercury is liberated.

Oxicyanide of mercury, $\text{Hg Cy} + \text{Hg O}$, appears when hydrocyanic acid of considerable strength (10 or 20 per cent) is agitated with red oxide of mercury in large excess, as a white powder intermixed with the red oxide. It is sparingly soluble in cold water, but may be dissolved out by hot water, and crystallizes on cooling in transparent four sided acicular prisms. When heated gently, it blackens slightly, and then explodes. (Mr. Johnston, Phil. Trans. 1839, p. 113).

Cyanide of mercury, when digested upon red oxide of mercury, dissolves a large quantity of it, and forms, according to M. Kuhn, a *tribasic cyanide of mercury*, $\text{Hg Cy} + 3\text{Hg O}$, which is more soluble in water than the neutral cyanide, and crystallizes with more difficulty in small acicular crystals.

Cyanide of mercury and potassium, $\text{KyCy} + \text{HgCy}$, is formed on dissolving cyanide of mercury in a solution of cyanide of potassium, and crystallizes in regular octohedrons. Cyanide of mercury forms also crystallizable double salts with other cyanides, such as the cyanides of sodium, barium, calcium, magnesium, &c. It also combines with chlorides, bromides, iodides, and also with several oxi-salts, such as chromate and formate of potash, $2(\text{KO}, \text{Cr O}_3) + \text{Hg Cy}$ and $\text{KO}, \bar{\text{F}} + \text{Hg Cy}$.

Sulphate of mercury, Mercuric sulphate, HgO, SO_3 ; 1867 or 149.6—It is formed by boiling 5 parts of sulphuric acid upon 4 parts of mercury, till the metal is converted into a dry saline mass. Sulphate of mercury is a white crystalline salt, neutral in composition, but which, like most of the neutral salts of mercury, cannot exist in solution. It gives a dense yellow powder when decomposed by water, and sulphuric acid is dissolved. This subsulphate is known as *turbith mineral*, a name applied to it by the old chemists, because it was supposed

to produce effects in medicine analogous to those of a root formerly employed, and known as *convolvulus turpethum*. The composition of turbith mineral is $\text{HgO}, \text{SO}_3 + 2\text{HgO}$ (Kane). Solution of ammonia converts both the neutral sulphate and turbith mineral into a heavy powder, which Dr. Kane names *ammonio-turbith*, and finds to be $\text{HgO}, \text{SO}_3 + \text{Hg}, \text{NH}_2 + 2\text{HgO}$. It is, therefore, analogous in composition to the yellow powder produced by the decomposition of white precipitate.

Nitrates of the red oxide of mercury, Mercuric nitrates.—The neutral nitrate cannot be crystallized, but it exists in solution, when chloride of mercury is precipitated by nitrate of silver. When red oxide of mercury is dissolved in nitric acid, or when the metal is dissolved in the same acid with ebullition, till a drop of the solution no longer occasions a precipitate in water containing a soluble chloride, a subnitrate is formed crystallizing in small prisms, which are deliquescent in damp air. Its composition is expressed by $\text{Hg O}, \text{NO}_5 + \text{HgO} + 2\text{HO}$. It is the only crystallizable nitrate of this oxide. Decomposed by water, this salt yields yellow subnitrate, which when washed in its preparation by warm, but not boiling water, is $\text{HO}, \text{NO}_5 + 3\text{HgO}$. When the subnitrate is prepared by boiling water, it has a red colour, and probably consists of $\text{NO}_5 + 6\text{Hg O}$ (Kane).

Nitrate of mercury affords several compounds when treated with ammonia. When a dilute, and not very acid solution of that salt is treated in the cold, by weak water of ammonia not added in excess, a pure milk-white precipitate appears, which is not granular, and remains suspended in the liquid for a considerable time. It was analyzed by G. Mitscherlich, and to distinguish it from some other salts containing the same constituents, I shall name it *Mitscherlich's ammonia subnitrate*. It contains $\text{NO}_5, 3\text{HgO}$ and NH_3 , which Dr. Kane would arrange thus, $\text{NH}_3, \text{NO}_5 + 3\text{HgO}$, making the ammonia or amide of hydrogen basic to the acid. The preceding compound is altered in its appearance by boiling water, and becomes much heavier and more granular forming *Soubeiran's ammonia subnitrate*, the composition of which Dr. Kane finds to be $\text{HgO}, \text{NO}_5 + \text{Hg}, \text{NH}_2 + 2\text{HgO}$; or it resembles in constitution the bodies already described containing chlorine and sulphuric acid. The *yellow crystalline ammonia subnitrate*, a third compound, was obtained by G. Mitscherlich by boiling the ammonia subnitrate with an excess of ammonia, and adding nitrate of ammonia by which a

portion of the powder is dissolved ; the solution, as it cools and loses ammonia, yields small crystalline plates of a pale yellow colour. The constituents of this salt are NO_5 , 2HgO and NH_3 . Dr. Kane doubles its equivalent and represents it as a compound of Soubeiran's salt with nitrate of ammonia, as it appears to be produced by the solution of the former salt in the latter, $(\text{HgO}, \text{NO}_5 + \text{Hg}, \text{NH}_2 + 2\text{HO}) + \text{NH}_4\text{O}, \text{NO}_5$. Soubeiran's ammonia subnitrate is dissolved in considerable quantity, when boiled in a strong solution of nitrate of ammonia and the solution deposits, on cooling, small but very brilliant needles, which were observed and analyzed by Dr. Kane. *Kane's ammonia subnitrate* is decomposed by water, nitrate of ammonia dissolving and Soubeiran's sub-salt being left undissolved. It contains the elements of $3(\text{NH}_4\text{O}, \text{NO}_5)$ and 4HgO . Dr. Kane believes that it is most likely to contain Soubeiran's subnitrate ready formed, which leaves 2 atoms of nitrate of ammonia and 2 atoms of water to be otherwise disposed of.*

Nitrate of mercury forms an insoluble compound with sulphuret of mercury, $\text{HgO}, \text{NO}_5 + 2\text{HgS}$, resembling the compounds of the sulphate and chloride with sulphuret of mercury. It also forms double salts with iodide and cyanide of mercury.

SECTION II.

SILVER.

Eq. 1351.6 or 108.3 ; Ag (argentum).

This metal is found in various parts of the world, and occurring often in the metallic state and being easily melted must have attracted the attention of mankind at an early period. Before the discovery of America, the silver mines of Saxony were of considerable importance, but the silver mines of Mexico and Peru far exceed in value the whole of the European and Asiatic mines ; the former have furnished during the last three centuries, according to Humboldt, 316 millions of pounds troy of pure silver.

A considerable quantity of silver is obtained from ores of lead by cupellation, as has already been described under that metal. The native silver, which is in the condition of threads or thin

* Trans. of the Royal Irish Academy, vol. xix. pt. I ; or, An. de Ch. et de Ph. t. 72, p. 225.

leaves, is separated from the gangue or accompanying rock, by *amalgamation*, a process which is also followed in the treatment of the most frequent ore of silver, the sulphuret, when it is not accompanied by sulphuret of lead. The last ore, ground to powder, is roasted in a reverberatory furnace with 10 per cent of chloride of sodium, by which the silver is converted into chloride. It is then introduced into barrels, with water, iron and a quantity of metallic mercury, and the materials kept in a state of agitation for eighteen hours by the revolution of the barrels on their axes. The chloride of silver, although insoluble, is reduced to the metallic state by the iron, and chloride of iron is produced, while the silver forms a fluid compound with the mercury. By adding more water and turning the barrels more slowly, the fluid amalgam separates and subsides. It is drawn off and subjected to pressure in a chamois leather bag; the mercury passes through the leather, while a soft amalgam of silver remains in the bag. The mercury is afterwards separated from this amalgam, by a species of distillation, *per descensum*, and the silver remains. Where machinery cannot be applied and iron is not used, the waste of mercury in the amalgamation is considerable. Mr. P. Johnston proposes to diminish the loss of mercury, as soluble chloride, which then occurs, by using an amalgam of zinc and mercury, instead of pure mercury.

Silver is obtained free from other metals and in a state of purity, for chemical and other purposes, in two different ways. 1. The metal is dissolved in pure nitric acid, slightly diluted, and precipitated by a solution of chloride of sodium; the salts of the other metals present remain in solution. The insoluble chloride of silver, thus obtained, is washed well upon a filter with hot water and dried. A quantity of carbonate of potash, equal to twice the weight of the silver, is fused in a crucible, and the chloride of silver gradually added to it; chloride of potassium is formed, and carbonic acid and oxygen escape with effervescence. The crucible is then exposed to a sufficient heat to fuse the reduced silver, which subsides to the bottom. 2. The mode of separating silver from the common metals, in the ordinary practice of assaying, is like many metallurgic operations, an exceedingly elegant and refined process. A portion of the silver alloy, the *assay*, is fused with several times its weight of pure lead (an alloy of 1 copper and 15 silver with 96 lead for instance) upon a bone-earth cupel, which is supported in a little oven or

muffle, heated by a proper furnace. Air being allowed access to the assay, the lead is rapidly oxidated, and its highly fusible oxide imbibed, as it is produced, by the porous cupel. The disposition of copper and other common metals to oxidate is increased by the presence of the lead, and their oxides, which form fusible compounds with oxide of lead, are removed in company with the latter. When the foreign metal is nearly entirely removed, the assay is observed to become rounder and more brilliant, and the last trace of fused oxide occasions a beautiful play of prismatic colours upon its surface, after which, the assay becomes, in an instant, much whiter, or *flashes*, an indication that the cupellation is completed.

Pure silver is the whitest of the metals, and susceptible of the highest polish; when granulated by being poured from a height of a few feet into water, its surface is rough, but its aspect peculiarly beautiful. It crystallizes in the cube and regular octohedron, both from a state of fusion and by precipitation from solution. Silver is in the highest degree ductile and malleable; its density varies between 10.474 and 10.542, it fuses at 1873° . When in the liquid state, it is capable of absorbing oxygen gas from the air, which is discharged again in the solidification of the metal, and gives rise to a sort of vegetation upon its surface, or even occasions the projection of small portions of the silver to a distance, an accident which is known in assaying as the *spitting* of the metal. Gay-Lussac observed that when a little nitre was thrown upon the surface of melted silver in a crucible, and the whole kept in a state of fusion for half an hour, a very considerable absorption of oxygen took place. When the crucible was removed from the fire and quickly placed under a bell jar filled with water, which can be done without danger, the silver discharged a quantity of oxygen equal to 20 times its volume. This property is possessed only by pure silver, it does not appear at all in silver containing 1 or 2 per cent of copper. As oxide of silver is reduced by a red heat, the absorption of the oxygen by the fluid metal must be a phenomenon of a different nature from simple oxidation.

Silver does not combine with the oxygen of the air at the usual temperature, nor even when heated; the tarnishing of polished silver in air is occasioned by the formation of sulphuret of silver. Silver does not dissolve in any hydrated acid, by substitution for hydrogen, but on the contrary, it is displaced

from a solution in an acid, by hydrogen and precipitated in the metallic state. This metal is also precipitated by mercury and all the more oxidable metals. Its salts are reduced at the usual temperature by sulphate of iron, of which the protoxide is converted into peroxide. But if the persulphate of iron be boiled upon the precipitated silver, the latter is dissolved again, and oxide of silver and protoxide of iron reproduced. Silver, however, is oxidated when fused or heated strongly in contact with substances for which oxide of silver has a great affinity, as with a siliceous glass, and stains the glass yellow. It is oxidated by concentrated sulphuric acid, with the escape of sulphurous acid. Silver is readily dissolved by nitric acid, with a gentle heat, and with much violence, at a high temperature, nitrate of silver is formed and nitric oxide escapes. Silver combines in three proportions with oxygen forming a suboxide, Ag_2O , protoxide AgO and peroxide AgO_2 .

Suboxide of silver, Ag_2O .—The existence of this oxide has only very recently been established beyond doubt by M. Wöhler. The pure protoxide of silver is completely reduced to the state of metal by hydrogen gas, at 212° ; but the oxide contained in citrate of silver loses only half its oxygen in the same circumstances, the suboxide being formed and remaining in combination with one half of the citric acid of the former salt. The solution in water of the suboxide salt is dark brown, and the suboxide is precipitated black from it by potash. When the solution of the subsalt is heated, it becomes colourless, and metallic silver appears in it. The salt dissolves of a brown colour in ammonia. Several other salts of silver, containing organic acids, comport themselves in the same way as the citrate, when heated in hydrogen.*

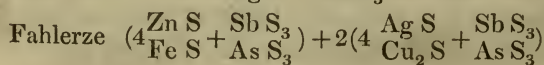
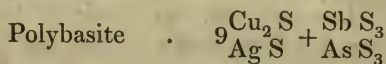
Protoxide of silver, AgO , 1451.6 or 116.3.—It is thrown down when potash or lime-water is added to a solution of nitrate of silver, as a brown powder, which becomes of a darker colour when dried. The powder was found to be anhydrous by Gay-Lussac and Thenard; its density is 7.143, according to Herapath. Oxide of silver is a powerful base, and forms salts, several of which have been found isomorphous with the corresponding salts of soda. It is soluble, like oxide of lead, to a small extent in pure water, free from saline matter, and the solution has an alkaline reaction. Oxide of silver is not dissolved

* Liebig's Annalen, vol. 30, p. 1, 1839.

by solutions of the hydrates of potash and soda. Its salts are precipitated black by sulphuretted hydrogen, and afford, when treated with hydrochloric acid or a soluble chloride, a white curdy precipitate, the chloride of silver, which soon becomes purple, if exposed, while humid, to the direct rays of the sun. This precipitate is not dissolved by nitric acid, but is dissolved by ammonia in common with most of the insoluble salts of silver.

Oxide of silver combines with ammonia and forms the fulminating *ammoniaret of silver*, a substance of a dangerous character from the violence with which it explodes. The ammoniaret may be formed by digesting newly precipitated oxide of silver in strong ammonia, or more readily by dissolving nitrate of silver in ammonia, and precipitating the liquor by potash in slight excess. If this substance be pressed by a hard body, while still humid, it explodes with unequalled violence; when dry, the touch of a feather is often sufficient to cause it to fulminate. The explosion is obviously occasioned by the reduction of the silver, from the combination of its oxygen with the hydrogen of the ammonia, and the evolution of nitrogen gas.

Sulphuret of silver, AgS , 1552.8 or 124.43.—Sulphur and silver may be combined together by fusion; the excess of sulphur escapes, and at a high temperature the sulphuret melts; it forms, on cooling, a crystalline mass. This compound has a lead-grey colour and metallic lustre. It is so soft that it may be cut by a knife, and is malleable. The sulphuret of silver is also remarkable for conducting electricity, like a metal, when warmed. The same compound occurs in nature, sometimes crystallized in octohedrons with their secondary faces. This sulphuret is particularly interesting from being isomorphous with the subsulphuret of copper, AgS with Cu_2S (page 144). These two sulphurets replace each other in indeterminate proportions in several double sulphurets of silver and other metals, as in *polybasite* and *fahlerze*, the composition of which may be expressed by the following formulæ, the symbols placed above each other, representing constituents, of which either the one or the other may be present:



Chloride of silver, Ag Cl , 1794.3 or 143.79.—This salt contains in 100 parts, 24.67 parts of chlorine, and 75.33 parts of silver. It is thrown down as a white precipitate, at first very bulky and curdy, when hydrochloric acid or a soluble chloride is added to any soluble salt of silver, except the hyposulphite. It is wholly insoluble in water, and the most minute quantity of hydrochloric acid contained in water may be detected by adding to it a drop of a solution of nitrate of silver. Hydrochloric acid, when concentrated, dissolves chloride of silver, which crystallizes from it in octohedrons, when the solution is evaporated. This salt dissolves easily in solution of ammonia, and crystallizes also as the ammonia evaporates. When heated, it fuses about 500° , forming a transparent yellowish liquid, which becomes, after cooling, a mass that may be cut with a knife and has considerable resemblance to horn; a property to which it was indebted for the name of *horn silver*, applied to it by the elder chemists. It is not volatile. Chloride of silver is not affected by a concentrated solution of potash. It is easily reduced to the state of metal by zinc or iron with water. Chloride of silver can be dissolved out in this way by means of zinc and acidulated water, from a porcelain crucible, in which it has been fused. The chloride and other salts of silver acquire a dark colour when exposed to light; chlorine escapes, and a portion of the salt appears to be reduced to the metallic state, as the blackened surface conducts electricity. According to Wetzlar, the black substance contains an inferior chloride of silver, and is not attacked by nitric acid, nor soluble in ammonia. Indeed, paper charged with chloride of silver is exceedingly sensitive to the impression of light, and has been employed to fix the image in the camera obscura. The unaltered chloride of silver in the paper, is afterwards dissolved out by a solution of hyposulphite of soda. Of anhydrous chloride of silver, 100 parts absorb 17.91 parts of ammoniacal gas, forming the compound $2\text{Ag Cl} + 3\text{NH}_3$. This compound loses its ammonia in the air. Chloride of silver is dissolved by concentrated and boiling solutions of chlorides of potassium, sodium and ammonium, and, on cooling, a double salt is deposited in crystals generally cubes. Chloride of silver is also dissolved by cyanide of potassium, and the solution yields a double salt by evaporation, (Liebig).

Bromide of silver, Ag Br . 2330 or 186.7.—This salt consists

in 100 parts, of 41.99 bromine and 58.01 silver. It is insoluble in water, and falls as a precipitate which is at first white, but becomes of a pale yellow on collecting. When fused and cooled, it gives a mass of a pure and intense yellow. It is soluble in ammonia and has most of the properties of chloride of silver.

Iodide of silver, Ag I , 2931.1 or 234.87.—This salt consists in 100 parts, of 53.89 iodine and 46.11 silver. It is insoluble in water, like the chloride, but is distinguished from that salt by its colour, which is pale yellow, by the difficulty with which it is dissolved in ammonia, and by being blackened more slowly by the action of light. According to Martini, 2500 parts of ammonia, of density 0.960, are required to dissolve one part of iodide of silver. It is soluble to a large extent, at the boiling temperature in concentrated solutions of the alkaline and earthy iodides, and forms with them double salts.

Cyanide of silver, Ag Cy , 1681.5 or 134.74.—This salt contains, in 100 parts, 19.62 cyanogen and 80.38 silver. It falls as a white powder when hydrocyanic acid is added to a solution of nitrate of silver. It is distinguished from chloride of silver by dissolving in concentrated nitric and sulphuric acids, when heated. It is readily decomposed by hydrochloric acid, and yields hydrocyanic acid, 100 parts of cyanide of silver giving 20.36 parts of hydrocyanic acid. It is decomposed by a red heat, and when well dried, gives nothing but cyanogen gas and silver. Cyanide of silver is dissolved by cyanide of potassium, and other soluble cyanides. The double cyanide of potassium and silver crystallizes in octohedrons, $\text{K Cy} + \text{Ag Cy}$.

Carbonate of silver, Ag O, CO_2 , is a white insoluble powder.

Sulphate of silver, Ag O, SO_3 , 1952.8 or 156.48.—It is obtained by dissolving silver with heat in concentrated sulphuric acid, or by precipitating a solution of nitrate of silver with sulphate of potash. It is soluble in 88 times its weight of boiling water, and crystallizes on cooling in the form of anhydrous sulphate of soda. This salt is highly soluble in ammonia, and gives, by evaporation, an ammoniacal sulphate of silver in fine transparent crystals, which are persistent in air; $\text{Ag O, SO}_3 + 2\text{NH}_3$. Chromate and seleniate of silver form analogous compounds with ammonia, which are all isomorphous. The bichromate of silver is also isomorphous with bichromate of soda.

Hyposulphate of silver, $\text{Ag O, S}_2 \text{O}_5$, is soluble in water, and

crystallizes in the same form as hyposulphate of soda. It crystallizes also with ammonia, as $\text{Ag O, S}_2 \text{O}_5 + 2\text{NH}_3$.

Hyposulphite of silver, $\text{Ag O, S}_2 \text{O}_2$.—Hyposulphurous acid appears to have a greater affinity for oxide of silver than for any other base. Oxide of silver decomposes the alkaline hyposulphites, and liberates one half of their alkali, and a double hyposulphite of the alkali and silver is formed. These double salts are best prepared by adding chloride of silver in small portions to the soluble hyposulphite of potash, soda, ammonia, or lime in the cold, till the liquid is saturated; after which, the solution is filtered, and mixed with a large quantity of alcohol, which precipitates the double salt; those of potash and soda are crystallizable. Herschel considers the double salts obtained in this manner, as probably containing one eq. of hyposulphite of silver, to two eq. of the other hyposulphite. The solution of one of these double salts dissolves more oxide of silver, and forms a double salt, which is believed to contain single equivalents of the salts, and precipitates as a white crystalline, pulverulent bulky mass. The second compound is sparingly soluble in water, but dissolves in ammonia, and communicates to the liquor an intensely sweet taste.

The hyposulphite of silver itself, is an insoluble substance; it is prone to undergo decomposition, changing spontaneously into sulphate and sulphuret of silver. When to a dilute solution of nitrate of silver, a dilute solution of hyposulphite of soda is added by small quantities, a white precipitate of hyposulphite of silver falls, which dissolves again in a few seconds, from the formation of the soluble double hyposulphite of soda and silver. When enough of hyposulphite of soda has been gradually added, to render the precipitate permanent, without, however, decomposing the whole silver salt, a flocculent mass is obtained of a dull grey colour, which is permanent. The liquor contains much hyposulphite of silver, and has an intensely sweet taste, not at all metallic; the silver is not precipitated from it by hydrochloric acid or the chlorides. An excess of hyposulphite of soda destroys the precipitated hyposulphite of silver, converting it into sulphuret of silver.

Nitrate of silver, Ag O, NO_5 , 2128.6 or 170.57.—When a piece of pure silver is suspended in nitric acid, it dissolves for a time without effervescence at a low temperature, nitrous acid being produced, which colours the liquid blue; but if heat be

applied or the temperature allowed to rise, then the metal dissolves with violent effervescence from the escape of nitric oxide. The nitrate of silver crystallizes on cooling in colourless tables, which are anhydrous. It is soluble in 1 part of cold, in $\frac{1}{2}$ part of hot water, and in 4 parts of boiling alcohol. The solution of this salt does not redden litmus paper, like most metallic salts, but is exactly neutral. Nitrate of silver fuses at 426° and forms a crystalline mass on cooling; it is cast into little cylinders for the use of surgeons. It is sometimes adulterated in this state with nitrate of potash, which may be detected by the alkaline residue which the salt then leaves, when heated before the blowpipe, or with nitrate of lead, when the solution of the salt is precipitated by iodide of potassium, of a full yellow colour. When applied to the flesh of animals, it instantly destroys the organization and vitality of the part. It forms insoluble compounds with many kinds of animal matter, and is employed to remove it from solution. When organic substances, to which a solution of nitrate of silver has been applied, are exposed to light, they become black from the reduction of the oxide of silver to the metallic state. A solution of nitrate of silver in ether is employed to dye the hair black. It forms also the indelible marking ink used to write upon linen. The part of the linen to be marked should be first wetted with a solution of carbonate of soda and dried, and the writing should be exposed to the light of the sun. For this ink, which is expensive, another liquid has been substituted by bleachers, namely coal tar, made sufficiently thin with naphtha to write with, which is found to resist chlorine and to answer well as a marking ink. A strong solution of nitrate of silver absorbs two equivalents of ammoniacal gas, and gives the crystallizable *Ammoniacal nitrate of silver*, $\text{Ag O}, \text{NO}_5 + 2\text{NH}_3$. The dry nitrate in powder absorbs three atoms of ammonia, $\text{NgO}, \text{NO}_5 + 3\text{NH}_3$.

Nitrate of silver forms a double salt with nitrate of the red oxide of mercury, which crystallizes in prisms. Nitrate of silver and cyanide of mercury also form a double salt, when hot solutions of them are mixed; $\text{Ag O}, \text{NO}_5 + 2\text{Hg Cy} + 8\text{HO}$. Cyanide of silver is soluble in a boiling solution of nitrate of silver, and gives a crystalline compound, $\text{Ag O}, \text{NO}_5 + 2\text{Ag Cy}$, which is decomposed by water.

Nitrite of silver, $\text{Ag O}, \text{NO}_3$ 1928.6 or 154.54.—Nitrate of

soda is fused at a red heat, till it is wholly converted into nitrite by loss of oxygen; the latter salt then begins to lose nitrous acid, and a small portion of the salt dissolved in water will be found to precipitate silver brown. The fusion is then interrupted, the salt dissolved in boiling water, precipitated by nitrate of silver, and filtered while still very hot. The nitrite of silver, which requires 120 times its weight of water at 60° to dissolve it, is precipitated as the solution cools. The other nitrites are prepared by rubbing this salt in a mortar with chlorides taken in equivalent quantities. It appears from experiments of Proust that two subnitrites of silver exist, one soluble and the other insoluble.

Acetate of silver, which is soluble in 100 times its weight of cold water, is precipitated when acetate of copper is mixed with a concentrated solution nitrate of silver. It crystallizes from solution in boiling water in anhydrous needles.

Oxalate of silver is an insoluble powder. A double *oxalate of potash and silver* is formed by saturating binoxalate of potash with carbonate of silver. It is very soluble, and forms rhomboidal crystals, which are persistent in air.

Peroxide of silver.—A superior oxide of silver is deposited upon the positive pole or zincoïd of a voltaic battery in a weak solution of nitrate of silver, in the form of needles of 3 or 4 lines in length, which are black and have a metallic lustre, while metallic silver is, at the same time, deposited in crystals upon the negative pole or chloroid. The former crystals are converted by sulphuric acid into oxide of silver and oxygen, and yield with hydrochloric acid, chloride of silver and chlorine.

Silver may be readily alloyed with most metals. It combines by fusion with iron, from which it cannot be separated by cupellation. Native silver is always associated with gold; the two metals are found crystallized together in all proportions in the same cubic or octohedral crystals. Gold may be detected in a silver coin, by dissolving the latter in pure nitric acid, when a small quantity of black powder remains, which after being washed with water, will be found to dissolve in nitromuriatic acid, giving a yellow solution in which protochloride of tin produces a precipitate of the purple powder of Cassius. Pure silver, being very soft, is always alloyed in coin and plate, with a certain quantity of copper, to make it harder. The

standard silver of England is an alloy of 222 pennyweights of silver with 18 pennyweights of copper. When the proportion of copper is considerable, the alloy becomes red by wear, shewing that the silver of the alloy yields more readily to attrition than the copper. This effect is very visible in the smaller silver pieces of some continental states.

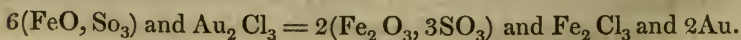
SECTION III.

GOLD.

Eq. 1243 or 99.6 ; Au (aurum).

Gold is found in small quantity in most countries, sometimes in iron pyrites, but generally native, massive and disseminated in threads through a rock, or in grains among the sand of rivers. It occurs crystallized in the cube and its allied forms. At present the principal supply of this metal is from the mines of South America, Hungary and of the Uralian mountains in Siberia. It is generally separated from earthy and all other metallic substances, except silver, by amalgamation. It may be separated from silver by nitric acid, which dissolves the latter metal, but only when it forms a large proportion of the alloy. When nitric acid does not dissolve the silver, the alloy is submitted to an operation termed *quartation* ; it is fused with four times its weight of silver, after which the whole silver may be dissolved out by nitric acid.

To obtain gold in a state of purity, the alloy containing it is dissolved in a mixture of two measures of hydrochloric, and one measure of nitric acid—a mixture which, from its application to dissolve gold has acquired the name of aqua regia. The solution of gold is evaporated by a water-bath, till acid vapours cease to be exhaled ; it is then dissolved in water and hydrochloric acid is mixed with it. On adding protosulphate of iron to this solution, the gold is wholly precipitated as a brown or brownish yellow powder, quite destitute of the metallic lustre, which, however, appears when the powder is rubbed. The protosulphate of iron is, at the same time, converted into persulphate and perchloride :



Gold is the only metal of a yellow colour. When pure, it is more malleable than any other metal, and nearly as soft as lead. Its ductility appears to have scarcely a limit. A single grain of gold has been drawn into a wire 500 feet in length, and this metal is beaten out into leaves which have not more than 1-200,000th of an inch of thickness. The coating of gold on gilt silver wire is still thinner. When very thin, gold is transparent, thin gold leaf allowing a green light to pass through it. The point of fusion of this metal is 2016° ; it contracts considerably upon becoming solid. The density of gold varies from 19.4 to 19.65, according as it has been more or less compressed. It does not oxidate or tarnish in air, at the usual temperature, nor when strongly ignited. But this and the other noble metals are dissipated and partly oxidated, when a powerful electric charge is sent through them in thin leaves. Gold is oxidated in contact with vitrifiable fluxes, and communicates to them a ruby colour. It is not dissolved by nitric, hydrochloric or sulphuric acid, nor indeed by any single acid. It is acted upon by chlorine, which converts it into perchloride, and by acid mixtures, such as aqua regia, which evolve chlorine. It combines in two proportions with oxygen, forming the two oxides Au_2O and Au_2O_3 , neither of which combines with acids.

Oxide of gold, Aurous oxide, Au_2O , 2586 or 207.21.—This oxide is obtained by decomposing the corresponding chloride of gold, by a cold solution of potash, as a green powder. It is partly dissolved by the alkali, and soon begins to undergo decomposition, being resolved into the higher oxide and metallic gold. The latter forms a thin film upon the sides of the vessel, which is green by transmitted light, quite like gold leaf.

Chloride of gold, Aurous chloride, Au_2Cl_3 , is obtained by evaporating a solution of the perchloride to dryness, and heating the powder thus obtained by a sand bath, retaining it about the temperature of melting tin and constantly stirring it, so long as chlorine is evolved. It is a white saline mass having a tinge of yellow, which is quite insoluble in water. In the dry state, it is permanent, but in contact with water it gradually undergoes decomposition, and is converted into gold and the perchloride. This change takes place almost instantaneously at the boiling temperature.

A corresponding *aurous sulphuret* is formed when sulphuretted

hydrogen gas is conveyed into a boiling solution of the perchloride of gold. It is dark brown, almost black.

Peroxide of gold, Auric oxide, Au_2O_3 , 2786 or 223.21.—This oxide has many of the properties of an acid. It is obtained by digesting magnesia in a solution of perchloride of gold, when an insoluble compound of auric oxide and magnesia is formed, which is collected upon a filter and well washed. The compound is afterwards digested in nitric acid, which dissolves the magnesia, with traces of auric oxide, but leaves the greater part of the latter undissolved. It is left in the state of a reddish yellow hydrate, which dried in air becomes chestnut brown. When precipitated by an alkali, auric oxide carries down a portion of the latter, of which it may be deprived by nitric acid. Dried at 212° it abandons its water, becomes black, and is in part reduced. When exposed to light, particularly to the direct rays of the sun, its reduction is very rapid. It is decomposed by an incipient red heat. Hydrochloric acid is the only acid which dissolves and retains this oxide, and then perchloride of gold is formed. It is dissolved by concentrated nitric and sulphuric acid, but precipitated from these solutions by water. The affinity of this oxide for alkaline oxides is so great, on the contrary, that when boiled in a solution of chloride of potassium, auric oxide is dissolved, and the liquid becomes alkaline; perchloride of gold with chloride of potassium, and *aurate of potash*, or a compound of auric oxide and potash, are formed. The compounds of auric oxide with the alkalies and alkaline oxides are nearly colourless, and are not decomposed by water. They appear to be of two different degrees of saturation, aurates which are soluble, and superaurates which are insoluble. The only one of these compounds which has been studied in some degree is the aurate of ammonia, or *fulminating gold* as it is named from its violently explosive character.

Aurate of ammonia.—When the solution of gold is precipitated by a small quantity of ammonia, a powder of a deep yellow is obtained, which is a compound of aurate of ammonia with a portion of perchloride of gold. This compound is exploded by heat, but the detonation is not strong. But when the solution of gold is treated with an excess of ammonia, and the precipitate well washed by ebullition in a solution of ammonia, or better in water containing potash, the fulminating gold has a yellowish brown colour with a tinge of purple. When dry,

it explodes most easily with a loud report, accompanied by a feeble flame. It may be exploded by a heat a little above the boiling point of water, or by the blow of a hammer. Its composition has not been certainly determined, but if the ammonia is present in double the proportion that would contain the hydrogen necessary to burn the oxygen of the auric oxide, which Berzelius considers probable, its constituents may be $\text{Au}_2\text{O}_3 + 2\text{NH}_3 + \text{HO}$. The affinity of auric oxide for ammonia is so great, that it takes that alkali from all acids. Thus, when auric oxide is digested in sulphate of ammonia, fulminating gold is formed, and the liquid becomes acid.

Purple of Cassius.—When protochloride of tin is added to a dilute solution of gold, a purple-coloured powder falls, which has received that name. It is obtained of a finer colour, when protochloride of tin is added to a solution of the perchloride of iron, till the colour of the liquid has a shade of green, and adding this liquid, drop by drop, to a solution of perchloride of gold which is free from nitric acid, and very dilute. After 24 hours, a brown powder is deposited, which is in a small degree transparent and purple-red by transmitted light. When dried and rubbed to powder, it is of a dull blue colour. Heated to redness it loses a little water, but no oxygen, and retains its former appearance. If washed with ammonia on the filter while still humid, it is dissolved, and a purple liquid passes through, which rivals the hypermanganate of potash in beauty. From this liquid, the colouring matter very gradually separates, weeks elapsing before the upper strata of the liquid become colourless, but it is precipitated more rapidly when heated in a close vessel between 140° and 180° . The powder of Cassius is insoluble in solutions of potash and soda. It may also be formed, by fusing together 2 parts of gold, $3\frac{1}{2}$ parts of tin and 15 parts of silver, under borax, to prevent the oxidation of the tin, and treating the alloy with nitric acid to dissolve out the silver; a purple residue is left containing the tin and gold that were employed.

The powder of Cassius is certainly, after ignition, a mixture of peroxide of tin and metallic gold, from which the last can be dissolved out by aqua regia, while the peroxide of tin is left; and the last mode of preparing it, favours the idea that its constitution is the same before ignition. But its property to dissolve in ammonia, and the fact that mercury does not dissolve

out gold from the powder when properly prepared, appear to me to be conclusive against that opinion. The proportions of its constituents vary so much, that there must be more than one compound, or more likely the colouring compound combines with more than one proportion of peroxide of tin. Berzelius proposes the theory that the powder of Cassius may contain the true protoxide of gold combined with the deutoxide of tin, $\text{AuO} + \text{Sn}_2\text{O}_3$, a kind of combination containing an association of three atoms of metal, which is exemplified in black oxide of iron, spinell, gahnite, franklinite and other minerals, and which we have repeatedly observed to be usually attended with great stability. A glance at its formula shews how readily the powder of Cassius, as thus represented, may pass into gold and peroxide of tin; $\text{AuO} + \text{Sn}_2\text{O}_3 \rightarrow \text{Au} + 2\text{SnO}_2$. The existence of a purple oxide of gold AuO is not established, but it is probably the substance formed when a solution of gold is applied to the skin or nails, and which dyes them purple. Paper coloured purple by a solution of gold becomes gilt when placed humid in phosphuretted hydrogen gas, which reduces the gold to the metallic state.

Sesqui-sulphuret of gold, Au_2S_3 , or the auric sulphuret, is formed when a dilute solution of gold is precipitated cold by sulphuretted hydrogen. It is a flocculent matter of a strong yellow colour, which becomes deeper by drying; it loses its sulphur at a moderate heat.

Sesqui-chloride of gold, *Perchloride of gold*, *Auric chloride*, Au_2Cl_3 , 3814 or 305.62.—It is formed when gold is dissolved in aqua regia. The solution is yellow, and becomes paler with an excess of acid, but is of a deep red when neutral in composition. It is obtained in the last condition by evaporating the solution of gold, till the liquid is of a dark ruby red colour, and begins to emit chlorine. It forms on cooling a dark red crystalline mass, which deliquesces quickly in air. But to procure the auric chloride perfectly free from acid salt, the only mode is to decompose the aurous chloride with water. A compound of chloride of gold and hydrochloric acid crystallizes easily from an acid solution, in long needles of a pale yellow, which are permanent in dry air, but run into a liquid in damp air. The solution of this salt deposits gold on its surface, and on the side of the vessel turned to the light. The gold is also precipitated in the metallic state by phosphorus, by most metals, the ferrous

salts, and many vegetable and animal substances, by vegetable acids, by oxalate of potash, when carbonic acid escapes. Chloride of gold is soluble in ether and in some essential oils. It forms double salts with most other chlorides, which are almost all orange when crystallized; in efflorescing, they become of a lemon yellow, but in the anhydrous state they are of an intense red. They are obtained by evaporating the mixed solutions of the two salts.

Chloride of gold and potassium, $\text{KCl} + \text{Au}_2 \text{Cl}_3 + 5\text{HO}$.—It crystallizes in striated prisms of right summits, or in thin hexagonal tables which are very efflorescent; this salt becomes anhydrous at 212° . The anhydrous salt fuses readily when heated, but loses chlorine and becomes a liquid, which is black while liquid, and yellow when cold. It is then a compound of the aurous chloride with chloride of potassium. *Chloride of gold and ammonium* crystallizes in transparent prismatic needles, which become opaque in air, Mr. Johnston found their composition to be $\text{NH}_4\text{Cl} + \text{Au}_2\text{Cl}_3 + 2\text{HO}$. *Chloride of gold and sodium* crystallizes in long four sided prisms, and is persistent in air. Its composition is $\text{Na Cl} + \text{Au}_2 \text{Cl}_3 + 4\text{HO}$. Bonsdorff has prepared similar double salts with chlorides of barium, strontium, calcium, magnesium, manganese, zinc, cadmium, cobalt and nickel. The salt of lime contains six and the salt of magnesia twelve atoms of water.

Sesquibromide of gold, $\text{Au}_2 \text{Br}_3$, is formed by dissolving gold in a mixture of nitric and hydrobromic acids. It greatly resembles the sesquichloride, and forms also an extensive series of double salts.

The *aurous iodide*, $\text{Au}_2 \text{I}$, is formed when hydriodic acid is digested upon peroxide of gold, iodine being, at the same time, liberated. It is a lemon yellow crystalline powder, insoluble in cold water, and soluble with great difficulty in boiling water.

The only salt with an oxygen acid, which peroxide of gold appears to form is the fulminate, and, perhaps, a seleniate.

ORDER IX.

METALS IN NATIVE PLATINUM.

SECTION I.

PLATINUM.

Eq. 1233.5 or 98.84. Pt.

This metal was discovered in the auriferous sand of certain rivers in America. Its name is a diminutive of *plata* silver, and was applied to it on account of its whiteness. It occurs in the form of rounded or flattened grains of a metallic lustre. It has been found in Brazil, Colombia, Mexico, St. Domingo, and on the eastern declivity of the Ural chain; it is everywhere associated with the debris of a rock easily recognized as belonging to one of the earliest volcanic formations.

The grains of native platinum contain from 75 to 87 per cent of that metal, so much iron that they are generally magnetic, from $\frac{1}{3}$ to 1 per cent of palladium, but sometimes much less, with small quantities of copper, rhodium, osmium and iridium. To separate the platinum from these bodies, the ore is digested in a retort with hydrochloric acid, to which additions of nitric acid are made from time to time. When the hydrochloric acid is nearly saturated, the liquid is evaporated in the retort to a syrup, then diluted with water and drawn off from the insoluble residue. If the mineral is not completely decomposed, more aqua regia is added and the distillation continued. A portion always remains undissolved, consisting of grains of a compound of osmium and iridium, and little brilliant plates of the same alloy, besides foreign mineral substances which may be mixed with the ore. The solution is generally deep red, and emits chlorine from the presence of perchloride of palladium; to decompose which, the liquid is boiled, chlorine escapes, and the palladium is reduced to protochloride. Chloride of potassium is then added, which precipitates the platinum as a sparingly soluble double chloride of platinum and potassium, of which the colour is yellow, but red if it is accompanied by the

double chloride of iridium and potassium. The precipitate is collected on a filter, and washed with a dilute solution of chloride of potassium. By igniting this double salt with twice its weight of carbonate of potash to the point of fusion, the platinum is reduced to the metallic state, while a portion of the iridium remains as peroxide. The platinum is dissolved by aqua regia in which the peroxide of iridium remains untouched. To complete the separation of the iridium, the precipitation, by chloride of potassium and ignition with carbonate of potash, may require to be repeated several times. But when it is not required to have platinum absolutely pure, the solution of the ore is precipitated by sal ammoniac, and it is in this way that much of the commercial platinum is procured, the insoluble double chloride of platinum and potassium is washed with a solution of sal ammoniac dried and heated to low redness; hydrochloric acid and nitrogen escape and sal ammoniac sublimes, while the platinum remains behind as a pulverulent mass, or spongy and a little coherent. The small trace of iridium which is left in commercial platinum increases greatly its hardness and tenacity.

Platinum is too refractory to be fused in our furnaces, but at a high temperature, its particles cohere like those of iron, and it may, like that metal, be welded. Hence, by heating a mass of the spongy platinum, previously strongly compressed, and submitting it to increasing pressure, the mass comes to be so far compacted, that it may be forged with a hammer. Platinum as it comes from the hands of the workman is highly malleable and ductile. It is the densest body at present known; the specific gravity of platinum was fixed by Dr. Wollaston at 21.53. This metal may be fused by the oxihydrogen blow-pipe, or even made to boil, and be dissipated with scintillations. It is not acted upon by any single acid, not even by concentrated and boiling sulphuric acid. Its resistance to the action of acids, conjoined with its difficult fusibility renders platinum invaluable for chemical experiments, and for some purposes in the chemical arts, particularly for the concentration of oil of vitriol.

The remarkable influence of a clean surface of platinum in determining the combustion of oxygen and hydrogen, has already been considered. This property platinum shares with osmium, iridium, palladium and rhodium. It is exhibited in the greatest degree by the highly divided metal, such as platinum sponge,

the condition in which the metal is left on igniting the double chloride of platinum and ammonium. Platinum precipitated from solution by zinc, causes the combustion of alcohol vapour. The *black powder of platinum* is the form in which that metal is most active. This is prepared by dissolving the protochloride of platinum in a hot and concentrated solution of potash, and pouring alcohol into it while still hot, by small quantities at a time; a violent effervescence occurs from the escape of carbonic acid gas, by which the contents of the vessel, unless capacious, may be thrown out. The liquor is decanted from the black powder which appears, and the latter boiled successively with alcohol, hydrochloric acid and potash, and finally four or five times with water, to divest it of all foreign matters. The powder, when dried, resembles lamp black, and soils the fingers, but still it is only metallic platinum extremely divided, and may be heated to full redness without any change of appearance or properties. It loses these, however, by the effect of a white heat, and assumes a metallic aspect. The powder of platinum, like wood charcoal, absorbs and condenses gases, in its pores, with the evolution of heat, a property which must assist its action on oxygen and hydrogen, although not essential to that action. When moistened with alcohol, it determines the oxidation of that substance in air, and the formation of acetic acid.

Platinum is insoluble in all acids, except aqua regia. It may be oxidated in the dry way by fusing it with hydrate of potash or nitre. Palladium, osmium and iridium resemble platinum in their chemical relations, the corresponding compounds of these four metals being isomorphous; platinum and iridium have also the same atomic weight. Of platinum, only two degrees of oxidation are known with certainty, the protoxide, Pt O , and peroxide Pt O_2 .

Protoxide of platinum, Platinous oxide, Pt O , 1333.5 or 106.84. —It is obtained by digesting the corresponding chloride of platinum with potash, as a black powder, which is a hydrate. This oxide is dissolved by the excess of alkali, and forms a green solution, which may become black like ink with a large quantity of oxide. Protoxide of platinum forms the platinous class of salts, which have a greenish, or sometimes red colour, and are distinguished from the platinic salts by not being precipitated by sal ammoniac.

Sulphuret of platinum, Pt S , is thrown down as a black pre-

cipitate, when the protochloride of platinum is decomposed by sulphuretted hydrogen. It may be washed and dried without decomposition.

Protochloride of platinum, Pt Cl , is obtained by evaporating a solution of the bichloride of platinum to dryness; triturating the dry mass and heating it in a porcelain capsule, by a sand bath at the melting point of tin, taking care to stir it, at the same time, so long as chlorine is evolved. It remains as a greenish grey powder, quite insoluble in water, and repelling that liquid so as not to be moistened by it. This chloride is not decomposed by sulphuric or nitric acid, but is partially soluble in boiling and concentrated hydrochloric acid. From the last solution, alkalis throw down a black precipitate of protoxide. When the calcination of the bichloride of platinum, at 420° or 460° , is interrupted before the whole chlorine is expelled, the residue gives to water a compound of a brown colour, so deep, that the liquid becomes opaque. This, Professor Magnus believes to be a combination of the two chlorides of platinum. A double *protochloride of platinum and potassium*, $\text{PtCl} + \text{KCl}$ is obtained on adding chloride of potassium to the solution of the platinous chloride in hydrochloric acid, and evaporating the liquid. The salt crystallizes in four sided red prisms, of which the form is the same as a corresponding salt of palladium; it is anhydrous. A protochloride of platinum and sodium also exists, but does not crystallize easily.

Ammoniacal protochloride of platinum, $\text{Pt Cl} + \text{NH}_3$, was obtained by Magnus, on adding solution of ammonia to the double protochloride of platinum and ammonium. A green salt precipitates after a time, which is entirely crystalline, insoluble in water, alcohol, hydrochloric acid and ammonia.

The green crystalline salt of Magnus is not decomposed or dissolved by boiling alkalis, nor by boiling sulphuric or hydrochloric acid; so that the ammonia or its elements are in an unusual state of combination. M. J. Gros, of Wesserling, has formed a singular class of compounds from it. When treated with hot concentrated nitric acid, the green salt is converted into a white crystalline powder, which dissolves easily in water, leaving half the platinum in the metallic state. The white salt is obtained by a second crystallization in flat prisms; it is named *nitrate of the chloramide of platinum* by Liebig. Neither the chlorine nor the platinum contained in this salt is precipitated

by the usual reagents. When a hot saturated solution of this salt is mixed with sulphate of soda, a corresponding sulphate of less solubility is deposited in small needles. A hydrochlorate is also obtained by adding hydrochloric acid to a boiling solution of the nitrate or sulphate, which crystallizes on cooling in octohedral crystals. By mixing a solution of the nitrate with a soluble oxalate, phosphate, tartrate, citrate, malate and saccharate, compounds of these acids with the same base were produced, which are all crystallizable and less soluble in the cold than the nitrate.*

These salts are represented as containing a substance Pt, $\text{Cl N}_2 \text{H}_6$, of the same character as ammonium :

Hydrochlorate	Pt, $\text{Cl N}_2 \text{H}_6 + \text{Cl}$.
Nitrate	Pt, $\text{Cl N}_2 \text{H}_6 \text{O} + \text{NO}_5$.
Sulphate	Pt, $\text{Cl N}_2 \text{H}_6 \text{O} + \text{SO}_3$.
Oxalate	Pt, $\text{Cl N}_2 \text{H}_6 \text{O} + \text{C}_2 \text{O}_3$.

M. Liebig also suggests another view, that these salts contain a salt of platinum, analogous to the bichloride, but in which the second atom of chlorine is replaced by amidogen, that is $\text{Pt} + \text{Cl} \cdot \text{NH}_2$. This salt is combined with chloride of ammonium, in the hydrochlorate; which thus becomes analogous to the bichloride of platinum and potassium, of which the new salt has the form. The nitrate, sulphate, and oxalate are compounds of nitrate, sulphate and oxalate of ammonia with the same salt $\text{Pt} + \text{Cl} \cdot \text{NH}_2$. This last view, which is so simple, is opposed by the fact that neither chlorine nor platinum is precipitated from these salts by the usual reagents. But this, I think, is not a sufficient ground for its rejection, considering how little many admitted double salts are affected by the reagents which precipitate the salts individually before their combination, such, for instance, as the double oxalate of chromium and potash.

Corresponding *platinous iodides* and *cyanides* have been formed. The platinous oxide has also been united with several acids, particularly sulphuric, nitric, oxalic and acetic acids; but none of these salts has been crystallized, except the oxalate.

Peroxide of platinum, Platinic oxide, Pt O_2 , 1433.5 or 114.84.
—By precipitating sulphate of platinum with nitrate of

* Gros, An. de Ch. et de Ph. t. 69, p. 204.

barytes, nitrate of platinum is obtained. One half of its oxide may be precipitated by soda, from the last salt, but when a larger quantity of alkali is added, a subsalt is thrown down. The precipitated oxide is hydrated, very bulky and resembles perfectly peroxide of iron precipitated by ammonia. When heated, it first loses its water, and becomes black, then its oxygen, and leaves metallic platinum. Peroxide of platinum combines with acids, and forms a class of salts, which are either yellow or reddish brown. It has also a decided affinity for bases, and forms insoluble compounds with the alkalies, earths and many metallic oxides. It forms also, like peroxide of gold, a fulminating ammoniacal compound, discovered by Mr. E. Davy.

Bisulphuret of platinum, Pt S_2 , is formed by adding a solution of bichloride of platinum, drop by drop, to a solution of sulphuret of potassium. It is dark brown and by desiccation becomes black. When dried in open air, a portion of its sulphur is converted into sulphuric acid, by the absorption of oxygen, and the mass becomes strongly acid.

Bichloride of platinum, Pt Cl_2 , 2119 or 169.78.—Is obtained by concentrating the solution of platinum in aqua regia, as a red saline mass, which becomes brown when deprived of its water of crystallization by heat. The solution of this salt when pure, is an intense and unmixed yellow; the red colour which it usually exhibits being due to iridium or to protochloride of platinum. Bichloride of platinum is soluble in alcohol, and the solution is used to separate potash in the analysis of a salt. The salt being first ignited, to expel ammonia, is dissolved in a minimum of water, and the solution mixed with chloride of platinum, a yellow granular precipitate falls, if the salt contains potash, which may be washed with diluted alcohol, and dried. One hundred parts of this salt are equivalent to 19.33 parts of potash, and to 40.39 of platinum.

Chloride of platinum and potassium, $\text{KCl} + \text{Pt Cl}_2$, is the salt which falls on mixing chloride of platinum with chloride of potassium or any other salt of potash. The crystalline grains of which it is composed are regular octohedrons. This salt is soluble to a certain extent in water, but is wholly insoluble in alcohol. It is anhydrous. A very intense bright red-heat is required for its complete decomposition. The double *chloride of platinum and sodium*, $\text{Na Cl} + \text{Pt Cl}_2 + 6\text{HO}$, crystallizes in beautiful transparent prisms of a bright yellow colour. It is

soluble in alcohol as well as in water. When a solution of this salt in alcohol is distilled till only one-fourth of the liquid remains, the solution when evaporated gives a salt containing the elements of ether, belonging to a class of compounds discovered by Professor Zeise, and known as the etherized salts of Zeise. The *chloride of platinum and ammonium* resembles the double salt of potassium. Bonsdorff has formed a large class of compounds of bichloride of platinum with the alkaline, earthy and metallic chlorides, in all of which the salts are united in single equivalents. The bromides and iodides of platinum have likewise been formed, and classes of double salts derived from them. Peroxide of platinum has also been combined with acids, but none of its salts, with the exception of the oxalate, obtained in a crystalline state.

SECTION II.

PALLADIUM.

Eq. 665.9 or 53.36; Pd.

This metal was discovered in 1803, by Dr. Wollaston. It is precipitated from the solution of the ore of platinum, after the removal by sal ammoniac of that metal, by a solution of cyanide of mercury, and is gradually deposited as a yellowish white flocculent powder, which is cyanide of palladium, and yields the metal when calcined.

In external characters, palladium closely resembles platinum. It is nearly as infusible, but can more easily be welded. The density of the fused metal is 11.3; after being laminated 11.8. At a certain temperature, the surface of palladium tarnishes and becomes blue from oxidation, but when more strongly heated, the oxide is reduced. It is very slightly attacked by boiling and concentrated hydrochloric and sulphuric acids. Palladium dissolves in nitric acid, communicating a brownish red colour to the acid, while no gas is evolved if the temperature is low, the nitric acid decomposed being converted into nitrous acid. Palladium dissolves with facility in aqua regia; its surface is blackened by the tincture of iodine, which has no effect upon platinum. This metal has a considerably greater affinity for oxygen than platinum. It forms two oxides, the protoxide of palladium Pd O , and the peroxide Pd O_2 .

Protoxide of palladium, Palladous oxide, Pd O, 765.9 or 61.36.—This oxide is obtained by dissolving palladium in nitric acid, evaporating the solution to dryness, and calcining the nitrate by a gentle heat. It forms a black mass, which dissolves with difficulty in acids. When carbonate of potash or soda is added in excess to a palladous salt, the hydrated protoxide precipitates of a very dark brown colour. This oxide is easily deprived of its water by heat, but a violent calcination is necessary to reduce it to the metallic state.

Protosulphuret of palladium, Pd S, is obtained by precipitation of a palladous salt by sulphuretted hydrogen, and is of a dark brown colour, or is prepared by the direct union of its elements.

Protochloride of palladium, Pd Cl, is prepared by dissolving palladium in hydrochloric acid, to which a little nitric acid is added, and evaporating the solution to dryness, to expel the excess of acid. The compound is a mass of a dark brown colour, which becomes black when made anhydrous by heat, and may be fused in a glass vessel. When heated in platinum vessels it becomes contaminated by the protochloride of that metal. When dissolved with chloride of potassium, it forms a double salt, $K Cl + Pd Cl$, which is soluble in cold, and considerably more so in hot water, and crystallizes in four sided prisms, of a dull yellow. Protochloride of palladium also combines with chloride of ammonium and chloride of sodium, and forms double salts, according to Bonsdorff, with most other chlorides. Protochloride of palladium forms two ammoniacal compounds; one of which is insoluble, greenish yellow and anhydrous, $PdCl + NH_3$.

Protocyanide of palladium, Pd Cy, is always formed when cyanide of mercury is added to a neutral solution of palladium, as a light coloured precipitate which becomes grey after drying. When the solution of palladium is acid no precipitate is formed, and when the solution contains copper, the precipitate has a green colour. Palladium appears to have a greater affinity for cyanogen than any other metal. The cyanide of mercury even is decomposed when boiled with protoxide of palladium, and cyanide of palladium formed. When this cyanide is dissolved in ammonia, and the excess of the latter allowed to escape by evaporation, a precipitate of brilliant, colourless, crystalline plates is formed, which appears to be ammoniacal cyanide of palladium.

Nitrate of palladium, Pd O, NO_5 , is formed by dissolving the metal in nitric acid; the solution dries up into a dark red saline mass. When an excess of ammonia is added to this salt, and the solution evaporated by a gentle heat, a colourless ammoniacal nitrate is deposited in rectangular tables.

Peroxide of palladium, *Palladic oxide*, Pd O_2 , 865.9 or 69.36. —To prepare this oxide, Berzelius recommends a solution of the hydrate or carbonate of potash to be added, by small quantities at a time, to the dry bichloride of palladium and potassium, mixing well after each addition. A yellowish brown powder separates, which is the hydrated peroxide, retaining a little alkali. Washed with boiling water, it loses the greater part of its combined water and becomes black. This oxide dissolves with difficulty in acids; the solutions are yellow. The corresponding bisulphuret of palladium has not been formed.

Bichloride of palladium, Pd Cl_2 , is obtained in solution, when protochloride is dissolved in concentrated aqua regia, and the solution only slightly heated. It forms a solution of so dark a brown as to appear black, which gives a red precipitate with chloride of potassium. When the solution is diluted or heated, chlorine gas is evolved, and protochloride of palladium reproduced. The double salt of this chloride and chloride of potassium is obtained by treating the double protochloride of palladium and potassium in fine powder with aqua regia, and evaporating the supernatant fluid to dryness. It forms a cinnabar red powder, in which little octohedral crystals can be perceived, both the palladic and palladous double chlorides being isomorphous with the corresponding compounds of platinum. When treated with hot water, this double salt emits chlorine, and is in a great measure decomposed. The salts of the peroxide of palladium are scarcely known.

SECTION III.

IRIDIUM AND OSMIUM.

Eq. 1233.5 or 98.84 ; Ir.

The black scales which remain when native platinum is dissolved in aqua regia, were discovered by Mr. Smithson Ten-

nant to contain these metals (Phil. Trans. 1804). The same alloy occurs in flat white metallic grains in native platinum. Iridium has also been observed in combination with about 20 per cent of platinum, crystallized in octohedrons, which are whiter than platinum, and are said to have a greater density, namely 22.66. Osmium and iridium are separated from each other, with considerable difficulty, by processes for which I must refer to the memoir of Wollaston (Phil. Trans. 1829, p. 8), or to Berzelius, (*Traité*, t. I, p. 415).

Iridium is obtained immediately from the chloride, by decomposing that salt with hydrogen at a gentle heat, or by exposing it alone to a very high temperature, in the form of a grey metallic powder, much resembling spongy platinum. It is one of the most refractory bodies known, not being fused by the oxyhydrogen blow pipe. Mr. Children, however, succeeded in fusing a portion of iridium into a globule, by the discharge of a very large voltaic battery. This globule was white and very brilliant, but still a little porous; its density was 18.68. Iridium becomes white and brilliant by strong ignition, without fusion, and is afterwards insoluble in acids. If reduced by hydrogen at a low temperature, it oxidates slowly when heated to redness, or when digested in aqua regia. This metal is generally rendered soluble by one or other of the following operations. It is calcined with hydrate of potash or nitre, or with a mixture of these salts, which gives a compound of deutoxide of iridium and potash. Or, the metal is reduced to a fine powder and intimately mixed with an equal weight of chloride of potassium or sodium, and the mixture heated to low redness in a stream of chlorine gas. The metal then combines with chlorine, and the double chloride of iridium and potassium or sodium is formed, which is soluble in water.

Oxides of iridium.—Iridium forms four compounds with oxygen, which are obtained by decomposing the corresponding chlorides. The *protoxide of iridium*, Ir O , is obtained from the chloride produced when iridium is heated in chlorine gas. Also by precipitating the double chloride of iridium and potassium ($\text{K Cl} + \text{Ir Cl}$) by carbonate of potash. The hydrate is then obtained of a greenish grey colour, which is soluble in an excess of the alkaline carbonate. This oxide is the base of a class of salts. The *deutoxide of iridium*, $\text{Ir}_2 \text{O}_3$, is formed when the metal is calcined with hydrate of potash or nitre, and

is the state of oxidation which iridium most readily assumes. Berzelius recommends as the best process for procuring it, to mix the double bichloride of iridium and potassium ($K Cl + Ir Cl_2$) with twice its weight of carbonate of potash, and to expose it to a low red heat. On dissolving out the alkaline salt, the deutoxide remains as a very fine powder, of a black colour with a shade of blue. A heat above the melting point of silver is required to expel the oxygen from this oxide. It is reduced to the metallic state by hydrogen gas at the usual temperature, which appears to arise from the oxide of iridium having the property, as well as the metal, to determine the oxidation of hydrogen, a reaction which causes the oxide to be heated to the temperature at which it is itself reduced by hydrogen. The hydrate of this oxide dissolves in acids and forms a particular class of salts, of which the solutions are sometimes of a very dark colour, resembling a mixture of water and venous blood. *Binoxide of iridium*, or iridic oxide, $Ir O_2$, has not been obtained in a separate state, but exists in a class of salts, from which this oxide is not precipitated by an alkali. *Peroxide of iridium*, $Ir O_3$, or susiridic oxide, is formed in small quantity when the alloy of osmium and iridium fused in nitre is digested in aqua regia. The double perchloride of iridium and potassium then formed yields a rose-red solution. The salts of the protoxide and peroxide afford blue and purple solutions when mixed, depending probably on the formation of one or more combinations of these oxides. The name iridium (from Iris) was applied to this metal, from the variety of colours which its preparations exhibit.

Sulphurets of iridium corresponding with the oxides of the same metal have been formed.

Chlorides of iridium.—The *protochloride*, $Ir Cl$, is formed when iridium in powder is heated to low redness in chlorine gas. As thus prepared it is insoluble in water, but slightly soluble in hydrochloric acid. It forms double salts with chlorides of potassium, ammonium and sodium. The *sesqui-chloride*, $Ir_2 Cl_3$, also forms double salts, but which are not crystallizable. The *bichloride of iridium* forms a double salt with chloride of potassium, in brilliant black octohedral crystals, corresponding with the bichloride of platinum and potassium. The bichloride of iridium and sodium is also isomorphous with the corresponding platinum salt.

Carburet of iridium.—When a coherent mass of iridium is held in the flame of a spirit lamp, black masses appear on its surface, which are a carburet, containing 19.83 per cent of carbon, or Ir C_4 . The carbon burns off readily in the air.

OSMIUM.

Eq. 1244.5 or 99.72; Os.

In the treatment of the alloy of iridium and osmium, the latter is separated as a volatile oxide, or osmic acid. To obtain the metal, a solution of osmic acid is mixed with hydrochloric acid, and digested with mercury in a well closed bottle at a temperature of 104° (40° cent.). The osmium is reduced by the mercury, and an amalgam formed, which is distilled in a retort till all the mercury and calomel formed are removed: osmium remains as a black powder without metallic lustre. When rendered coherent, osmium is a white metal, less brilliant than platinum, and very easily pulverised. Its density is about 10. As obtained from the amalgam, osmium is highly combustible; when a mass of it is ignited at a point, it continues to redden, and burns without residue, being converted into the volatile oxide or osmic acid. Osmium in the same condition is oxidated by nitric acid or aqua regia, and the osmic acid formed distils over with the water and acid. But after being exposed to a red heat, osmium becomes much less combustible in air, and is not oxidated by the humid way, resembling silicon and titanium in that respect. Five different oxides of this metal are enumerated, but osmic acid is the only one of these which is formed directly; the others are obtained by the decomposition of corresponding chlorides. The three lowest of these oxides are analogous in composition to the oxides of iridium.

Chlorides and oxides of osmium.—When osmium is heated in a long glass tube by a spirit lamp and chlorine gas passed over it, two chlorides are formed, which condense separately in the tube, owing to a difference in their volatility. The *protochloride*, Os Cl , which is the least volatile, crystallizes in needles of a deep green colour. It is deliquescent, and forms a green solution remarkable for its beauty. This solution is instantly discoloured by great dilution, metallic osmium is deposited, and hydrochloric and osmic acids remain in solution. Chloride of

osmium combines with alkaline chlorides, and acquires greater stability. The *protoxide* is obtained by adding potash to a solution of this double salt; after some hours, a deep green, almost black, powder is precipitated, which is the hydrated oxide. This hydrate contains alkali. It dissolves slowly but completely in acids, and gives solutions of a deep green colour.

Deutoxide of osmium, Os_2O_3 , is obtained by heating a solution of the osmiate of ammonia to 100° or 140° , when nitrogen gas is disengaged and deutoxide deposited. The oxide contains ammonia. It dissolves slowly in acids, and forms yellowish brown solutions, which become of a brown black when they contain much oxide. The metal is not precipitated from these solutions by zinc or iron. The corresponding *sesquichloride of osmium* is obtained in combination with chloride of potassium, as a double salt, when the preceding oxide containing ammonia is dissolved in hydrochloric acid, and evaporated to dryness; the compound is not crystalline.

Bichloride of osmium, Os Cl_2 , is the more volatile chloride produced when osmium is heated in chlorine. It condenses as a dark red floury powder. Exposed to air, it attracts a little moisture, and forms dendritic crystals. This salt is soluble in little water, giving a yellow solution, but is decomposed by a large quantity, like the protochloride. The bichloride of osmium and potassium is prepared in the same manner as the corresponding salt of iridium. In powder, it is of a red colour like minium, but forms also the usual octohedral crystals, $\text{KCl} + \text{OsCl}_2$, which are brown. A solution of this double salt, mixed with carbonate of potash or soda, affords after a time, or immediately, if heated, the corresponding *peroxide of osmium*, Os O_2 , as a brown powder, which appears black when collected. It is a base capable of uniting with acids at the moment of its formation. This oxide like the peroxide of iridium is reduced by hydrogen at the usual temperature.

Osmic acid, Os O_4 , or the volatile oxide of osmium is best obtained by the combustion of osmium in a glass tube through which a stream of oxygen gas is passed. It condenses in long colourless, regular prismatic needles. The odour of this compound is extremely acid and penetrating, resembling that of the chloride of sulphur. It was from this property of its acid, which is so constantly observed when the oxidable compounds of osmium are heated in air, that osmium obtained

its name (from *ὀσμος* odour). Its taste is acrid and burning, but not acid. It becomes soft like wax by the heat of the hand, melts into a colourless liquid like water considerably below 212° , and enters into ebullition a very little above its point of fusion. It is dissolved slowly, but in considerable quantity, by water. The solution has no acid reaction. Osmic acid is also soluble in alcohol and ether, but these solutions are apt to deposit metallic osmium. It is a weak acid, being incapable of displacing carbonic acid from the carbonates, in the humid way, but forms a class of salts, the osmiates. Osmic acid is expelled by heat from most of its combinations with bases. A *terchloride of osmium* has been obtained in combination with chloride of ammonium, as a double salt, when osmic acid is saturated with that alkali, and treated, after a time, with an excess of hydrochloric acid, mercury being also placed in contact with it. After a few days, the liquid loses the odour of osmic acid, and when evaporated to dryness leaves the double salt, in brown dendritic crystals. The oxide corresponding with this chloride, Os O_3 is hypothetical. It cannot be extracted from the above ammoniacal compound, for when an alkali is added to it, ammonia which is set free immediately reduces the precipitated oxide to the state of deutoxide.

Sulphurets of osmium.—Osmium has a great affinity for sulphur, burning in the vapour of that substance, and appears to have as many degrees of sulphuration, as it possesses oxides.

SECTION IV.

RHODIUM.

Eq. 651.4 or 52.2; R.

This metal was discovered, by Wollaston, in the ore of platinum. He found the ore from Brazil to contain 0.4 per cent; native platinum from another locality has been found with so much as 3 per cent of rhodium.

After the precipitation of the palladium from the solution of native platinum, by cyanide of mercury, the solution, in order to obtain the rhodium, may be mixed with a little hydrochloric acid, and evaporated to dryness. The cyanide of mercury in excess is decomposed by the hydrochloric acid,

and converted into chloride of mercury. The dried mass is reduced to a very fine powder, and washed with alcohol of density 0.837, which takes up the double chlorides of sodium with platinum and iridium, the copper and mercury, but leaves the double chloride of rhodium and sodium in the form of a fine deep red powder. The rhodium is most easily reduced by gently heating the double chloride in a stream of hydrogen gas, and afterwards washing out the chloride of sodium by water.

Rhodium when rendered coherent, is a white metal like platinum, of which the density is about 11. It is brittle and very hard, and may be reduced to powder. When pure, it is not dissolved by any acid. But when alloyed with certain metals, such as platinum, copper, bismuth or lead, and exposed to aqua regia, it dissolves along with those metals. When fused with gold or silver, however, it is not dissolved with the other metal. But the most eligible mode of rendering rhodium soluble, is to mix it in fine powder with chloride of potassium or sodium, and to heat the mixture to low redness in a stream of chlorine gas. A double chloride is then formed, as with the other platinum metals in similar circumstances, which is very soluble in water. The solutions of rhodium have a beautiful red colour, the circumstance from which the metal derives its name (from *ῥόδον*, a rose). Rhodium may also be rendered soluble in the dry way, by fusing it with bisulphate of potash, when the metal is oxidated with the escape of sulphurous acid gas. Rhodium is the most oxidable of the platinum metals, combining with oxygen when heated to redness in an open vessel, and very readily when in fine powder and heated to a cherry red heat. It appears to form two oxides, the rhodous and the rhodic, of which, however, the last only has been isolated.

Oxides of rhodium.—Rhodic oxide, R_2O_3 , is produced when the metal is ignited with hydrate of potash and a little nitre, in a silver crucible. The metal swells up and becomes of a coffee brown, it is then a compound of rhodic oxide and potash, which must be washed with water and afterwards digested in hydrochloric acid; the hydrated oxide remains of a grey colour with a shade of green and insoluble in acids. The same hydrated oxide, as obtained from the double chloride of rhodium and potassium or sodium by precipitation with an alkali and evaporation, dissolves slowly in acids, with a certain quantity of alkali which is attached to it, assuming a yellow colour and producing

double salts. The solution in hydrochloric acid is also pale, although it contains chloride of potassium, while a solution of the double chloride prepared in the way formerly mentioned is a fine red. Hence Berzelius infers that there are two isomeric modifications of this oxide, of which the combinations, when in solution, are respectively yellow and rose coloured. The hydrated rhodic oxide contains one atom of water, $R_2O_3 + HO$; two compounds of rhodic oxide with a protoxide of the same metal or rhodous oxide, appear to exist, $R_2O_3 + 3RO$ and $R_2O_3 + 2RO$. The known compounds of rhodium are not isomorphous with compounds of platinum, but this may arise from these two metals affecting combination in different proportions, so that their compounds are not analogous in composition. Their association and resemblance in other respects afford a strong presumption of their being isomorphous bodies.

Sulphuret of rhodium.—Rhodium may be united with sulphur by either the dry or humid way. The sulphuret of rhodium was used by Wollaston to obtain the metal in a coherent mass.

Chloride of rhodium, R_2Cl_3 is obtained from the double chloride of rhodium and potassium, by precipitating the latter metal by fluosilicic acid. The dry salt is of a brown black and not crystalline, it requires a pretty high temperature to decompose it, and then resolves itself at once into chlorine and rhodium. This salt deliquesces in air; its solution in water is of a beautiful red colour. It appears to exist in combination with a protochloride of rhodium, in the rose red powder obtained by heating rhodium in a stream of chlorine, $R_2Cl_3 + 2RCl$. The double *chloride of rhodium and potassium*, prepared by the action of chlorine upon a mixture of rhodium and chloride of potassium, is $2KCl + R_2Cl_3 + 2HO$. It retains this water at 212° , but loses it at a higher temperature, this salt rarely crystallizes well, but its crystals according to Wollaston, are rectangular four sided prisms, terminated by four sided pyramids. The formula of the double *chloride of rhodium and sodium* is $3NaCl + R_2Cl_3 + 18HO$; it forms large prismatic crystals. Their solution is of a beautiful rose colour.

A *sulphate of rhodium* is formed when rhodium is ignited with bisulphate of potash, it gives a yellow solution. Another sulphate in combination with sulphate of potash gradually falls as a white powder, when sulphurous acid is added to a solution

of the double chloride of these bases. It is nearly insoluble in water, its formula is $\text{KO}, \text{SO}_3 + \text{R}_2\text{O}_3, 3\text{SO}_3$. The *nitrate of rhodium* is formed by dissolving the oxide in nitric acid. It forms a deliquescent salt of a dark red colour, $\text{R}_2\text{O}_3 + 3\text{NO}_5$; the last salt combines with nitrate of soda, forming dark red crystals soluble in water but not in alcohol, $\text{NaO}, \text{NO}_5 + \text{R}_2\text{O}_3, 3\text{NO}_5$.

PART III.

ORGANIC CHEMISTRY.

CHAPTER I.

SECTION I.

PRELIMINARY OBSERVATIONS.

By organic substances are meant definite chemical compounds, found ready formed in organized beings, and their modifications produced by artificial processes which may be greatly varied. These substances are known to be definite in composition when they are crystallizable, or when they enter into compounds that are crystallizable; or have, if liquid, a fixed boiling point. In their number, which has been vastly increased by late researches, are found many acids, several alkaline bodies, and a large class of neutral substances which cannot be assimilated to any class of inorganic compounds. Recent inquiries have disclosed some unexpected relations between different organic substances, and supplied the means of associating groups of them from similarity of composition. There is the same evidence of the existence in these substances of compound radicals, which may be transferred from a state of combination with one element to another, as in the compounds of the inorganic kingdom allowed to contain such constituents; although the organic radicals cannot be isolated and exhibited in a separate state, except perhaps in a single instance. The radicals most characteristic of organic compounds, hitherto investigated, are of the basyle class, bodies resembling therefore the metallic elements in their functions and the series of compounds with salt radicals which they are capable of forming. Of all these hypothetical radicals ammonium has served as the prototype; they are allowed how-

ever to differ in one respect from ammonium and the metals, namely in combining readily with hydrogen, which element acts towards them as a salt-radical. The supposed prevalence of such radicals in the constitution of organic compounds has led M. Liebig to define organic chemistry as *the chemistry of compound radicals*; the whole of which indeed as are of a basyle character, including ammonium itself, may be properly assigned to this department of the science.

Many organic substances are highly complex and contain a large number of atoms; a circumstance which renders them very liable to change, and has led to the observation of peculiar modes of decomposition among organic compounds, indicating novel modes of the action of chemical affinity.

COMPOSITION OF ORGANIC SUBSTANCES, AND METHOD OF ANALYSIS.

The elements which usually enter into organic substances are few in number, namely carbon, hydrogen, oxygen and nitrogen. Some organic substances contain only carbon and hydrogen, as olefiant gas and other hydro-carbons; more frequently carbon, hydrogen and oxygen, as sugar, gum, many neutral bodies, and most organic acids. To these a fourth element is added, nitrogen, in the vegeto-alkalies and various other compounds which belong more usually to the animal than vegetable division; indeed carbon prevails in the organic world, as silicon does in the mineral, and as most minerals are silicates, so organic substances are the compounds of carbon. To these elements certain others are occasionally added, although most usually by artificial processes, as chlorine in the place of hydrogen, and sulphur, phosphorus, arsenic or tellurium in that of oxygen. The elementary analysis of organic matters is determined with much exactness, and by means so simple and rapid of execution as to render an ultimate analysis often the most ready test of the purity of a substance. The process followed, consists in burning the matter to be analysed by means of oxide of copper, so as to convert its carbon into carbonic acid and its hydrogen into water, which are both collected and weighed; when the matter contains nitrogen, the latter is collected in the form of gas. The oxygen, which the matter contains,

is represented by the excess of its weight over the sum of the weights of the carbon, hydrogen and nitrogen found. I shall merely sketch the outline of this fundamental and highly important process, referring for the minute instructions necessary for its exact execution to Professor Liebig's valuable tract on Organic Analysis.*

The nitrate of copper, decomposed by a red heat in an earthenware crucible, gives a fine light oxide, very suitable for the combustion process, and of which a considerable quantity must be provided. It is a property of this oxide to be reduced with extreme facility at a red heat, by carbon or hydrogen, and at the same time to resist an intense temperature, when heated apart from combustible matter, without losing a particle of oxygen. The substance to be analysed, or burnt with oxide of copper, we shall suppose to be sugar.

The tube for combustion is of the most difficultly fusible glass, free from lead; no variety answers better for it than the white Bohemian glass. It is generally about 0.4 inch in internal diameter, and 14 or 15 inches long, drawn out, bent and

FIG. 85.



sealed at one end, as represented (Figure 85,) and open at the other. To have

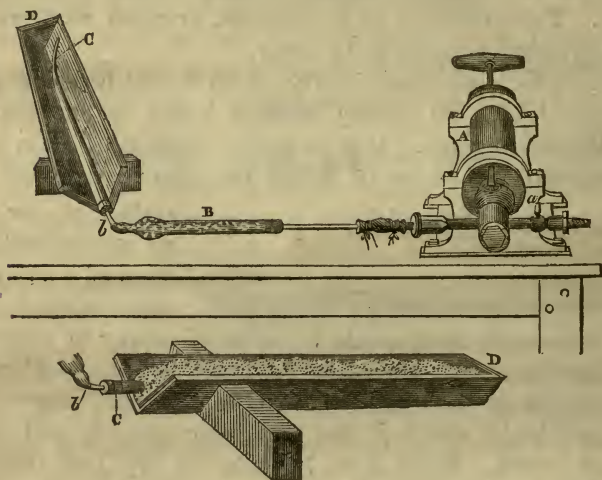
some measure of the quantity of oxide of copper to mix with the substance to be analysed, the tube is to be filled to three fourths of its length with pure oxide of copper, out of a crucible in which it has just been ignited, and while it is yet warm. From 5 to 7 grains of dry loaf sugar in fine powder are first rubbed in a porcelain mortar with a little oxide, with which it is intimately mixed, and by degrees the whole oxide of copper is added, which was measured in the tube. Having first introduced pure oxide of copper, so as to fill about half an inch at the closed end of the tube, the mixture from the mortar is then introduced, followed by a portion of oxide employed to rinse out the mortar, and the last covered by pure oxide, so as to fill up the tube to within one inch of

* Translated by Dr. W. Gregory, and forming Part I of Griffin's Scientific Miscellany. Tegg, London.

its open extremity. The lengths occupied by the different layers of pure oxide, mixture, rinsings of mortar and again pure oxide are indicated by dotted lines in the figure. The weight of the whole oxide of copper used generally exceeds 1200 grains.

In these operations, the oxide of copper inevitably absorbs a quantity of moisture from the air, which may amount to 0.2 or 0.3 grain, and which coming off afterwards during the ignition would vitiate the determination of the hydrogen. The tube and oxide must therefore be dried by a heat which will not decompose the sugar. This is done by placing the com-

FIG. 86.



bustion tube C, in a wooden trough D, (Fig. 86) and covering it with sand of the temperature of 250° ; connecting it at the same time by a perforated cork *b*, with a tube B, containing fragments of chloride of calcium, and an exhausting syringe A. By means of the latter, air and moisture are withdrawn from the combustion tube, the moisture being retained by the chloride of calcium in B; air is then admitted to C by the stopcock *a*, and withdrawn again by the syringe ten or twelve times. The mixture may then be considered dry.

The furnace for the combustion is made of sheet iron of a

FIG. 87.

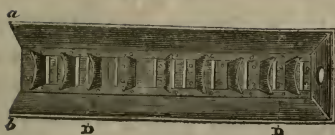
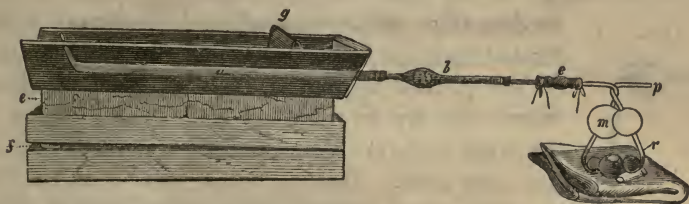


FIG. 88.



trough form (Fig. 87), 22 to 24 inches long and 3 inches high. The bottom is 3 inches wide, with narrow apertures about half an inch apart, which form a sort of grate; the sides of the furnace are inclined outwards, and $4\frac{1}{2}$ inches apart at top. To support the combustion tube, pieces of strong sheet iron of the form D, (Fig. 88), are rivetted to the bottom of the furnace, at intervals; they are of exactly equal height, with their edges ground flat, and correspond with the round aperture in the front of the furnace, A. The furnace rests upon two thin bricks supported upon two blocks of wood, which are separated a little by a wedge, so as to elevate slightly the further end of the furnace as in Fig. 89.

FIG. 89



When the heat is to be increased, the furnace is raised a little on one side, by a thin bit of tile placed below. Good charcoal, is the fuel employed in this furnace; the combustion may be animated by fanning the burning embers with a square piece of pasteboard; which is safer than raising the furnace off the bricks. Immediately connected with the combustion tube, by means of a perforated cork, is a tube of the form *b* (Fig. 89), containing fragments of strongly dried, but not fused chloride of calcium. In this tube is condensed the water formed in the combustion, of which the weight is ascertained by weighing the tube, before and after the combustion. Beyond the chloride of calcium tube and connected with it by a short caoutchouc tube, *c*, is a glass instrument *p m r*, containing a strong solution of caustic potash, of density 1.25 to 1.27, for the ab-

sorption of the carbonic acid produced in the combustion, This instrument consists of five balls, of which *m* is larger than the others; no more of the potash ley is put into it than fills the three central bulbs, leaving a bubble of air in each. One corner is elevated a little by a cork placed under it, and the whole supported upon a folded towel; the potash apparatus, when filled with ley, commonly weighs from 750 to 900 grains. This apparatus is also weighed before and after the combustion, and the increase ascertained.

Before introducing the combustion tube into the furnace, it must be tapped smartly in a horizontal position, so as to produce a vacant space above the oxide of copper through the whole length of the tube, by which the gaseous products may escape (Fig. 85). The same precaution must be taken in the preparatory operation of drying the oxide of copper, otherwise it often happens that a portion of the oxide is thrown forwards out of the tube. Before beginning the combustion, it is necessary to ascertain that all the joinings are tight, by sucking out a bubble or two of air from the apparatus, by means of the

FIG. 90. suction tube (Fig. 90), applied by means of a perforated cork not fitting very tightly to the open end of the potash apparatus. The slight exhaustion causes the ley to stand $1\frac{1}{2}$ or 2 inches higher in the inner limb *m* of the potash apparatus than in the outer limb. This elevation will be maintained if no air enters by the cork or caoutchouc joint,

and the apparatus is then certainly tight, but not so if the level changes and the liquid falls back into the middle part of the apparatus.

In conducting the combustion, the anterior portion of the tube, containing only oxide of copper, is first surrounded by red hot charcoal. The fragments of charcoal are kept in their place and the heat prevented from spreading, by a screen,

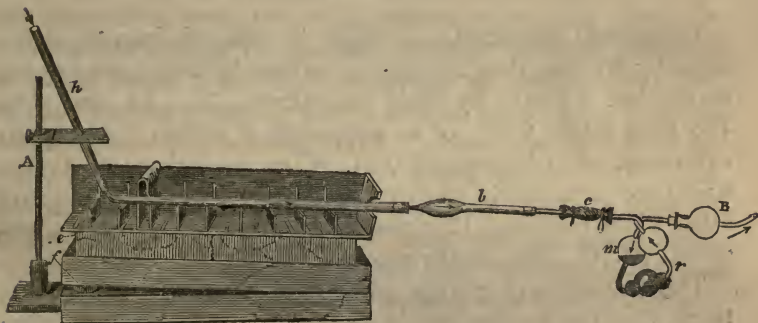
FIG. 91. (Fig. 91) of sheet iron, of the same width as the furnace. This screen is slowly moved backwards, by half an inch to an inch at a time, and the fire space immediately filled up with red hot charcoal, so as to raise rapidly the portion of tube newly exposed to a red heat. A screen (Fig. 92) should be placed upon the front



FIG. 92. of the furnace, to prevent the cork being burned and the chloride of calcium tube being heated, by radiation from the furnace. But the fore end of the tube, which is empty and projects an inch beyond the furnace, should be kept so hot during the whole operation that no water condenses in it; in the course of twenty minutes or half an hour the screen has been moved to the end of the tube, and the combustion completed. When the evolution of gas stops all at once, the combustion is certainly complete, and a good result is obtained; the tube should be heated red hot, but not to bright redness; it begins to stick to the supports when heated too hot.

As soon as the evolution of gas terminates, the potash ley begins to rise into the bulb *m*. The pointed extremity of the combustion tube should then be broken by means of a pair of pliers, after removing the charcoal from that end of the furnace. An open tube *h*, 12 or 15 inches long, is then placed over the opened end, and supported by a stand, (Fig. 93), while by

FIG. 93.



means of the suction tube *B*, a certain quantity of air is drawn by the mouth through the potash apparatus. The whole watery vapour and carbonic acid remaining in the combustion tube, are thus brought into the chloride of calcium tube and potash apparatus, and completely absorbed.

The data furnished by the combustion afford the means of calculating the composition of the substance analysed, as the composition of water and carbonic acid is known, the former

consisting of 1 hydrogen and 8 oxygen in 9 parts, and the latter of 27.675 carbon and 72.325 oxygen in 100 parts:

The hydrogen is one ninth of the increase of weight in the chloride of calcium tube.

The carbon is 27.67 per cent of the increase of weight in the potash bulbs.

The oxygen is the quantity obtained by adding the weights of the hydrogen and carbon together, and deducting their sum from the weight of matter originally employed.

The following are the details of a particular analysis of sugar (Dumas).

Weight of Sugar. . . .	600
Weight of Carbonic Acid. . . .	921
Weight of Water. . . .	353

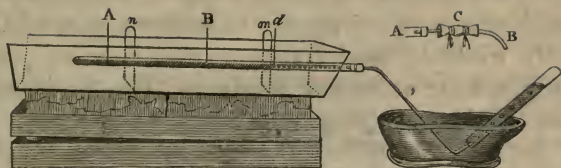
These give by calculation :—

Carbon. . . .	254.6..42.4
Hydrogen. . . .	39.2.. 6.5
Oxygen. . . .	306.2..51.1
	<hr/>
	600 ..100

The atomic constitution of sugar is obtained from these results, by dividing the quantities of carbon, hydrogen and oxygen in the last column, by their equivalents, 76, 12.5 and 100. We thus obtain 0.558 of an equivalent of carbon, 0.520 of an equivalent of hydrogen and 0.511 of an equivalent of oxygen, which are more nearly proportional to the following than any other whole numbers, 12 carbon, 11 hydrogen, 11 oxygen; and give $C_{12}H_{11}O_{11}$, the usually received formula for cane sugar.

The estimation of nitrogen, when present in an organic substance, requires another combustion in which that gas is determined by measurement. This gas generally escapes in a free state, mixed with the carbonic acid and watery vapour; but frequently deutoxide of nitrogen is formed, which renders the determination of the nitrogen difficult; to decompose the latter it is necessary to have a portion of copper turnings in the anterior part of the tube, which are kept at a full red heat during the combustion, as from the screen *m* (Fig. 94) to the mouth of the tube. This is followed by a layer of pure oxide from *m* to B, and then the mixture from B to A; as soon as the copper

FIG. 94.



and oxide are at a red heat, the tube is heated from the closed end, a second screen *n* being gradually advanced from that extremity. When the proportion of nitrogen is not inconsiderable, it is generally sufficient to determine its relation by volume to the carbonic acid evolved at the same time. This is done by attaching a bent quill tube (Fig. 94) to the mouth of the combustion tube, by which the gas evolved is conveyed to the mercurial trough, and collected at different stages of the combustion in a small graduated jar. By passing up a few drops of caustic potash into the gas in the jar, the carbonic acid is absorbed and the nitrogen remains. If the proportion between the volumes of the two gases thus observed is the same in several successive trials, and no red nitrous fumes be perceived on mixing the gas with air, this result is sufficient for the nitrogen. The whole quantity of carbonic acid produced in the combustion being known from a previous analysis conducted in the usual way, we can obtain the volume of nitrogen by calculation, and thence its weight. Or, as two volumes of carbonic acid and of nitrogen represent both one atom of carbon and nitrogen, the atoms of these two gases are in the same number as the volumes observed; consequently when the weight of the carbonic acid is known, that of the nitrogen may be calculated from the atomic weights of carbonic acid and nitrogen.

For the analysis of uric acid, in which the volumes of the nitrogen and carbonic collected are as 4 to 10, and of bitartrate of ammonia in which they are as 1 to 8, this method answers very well, but when the proportion of nitrogen is smaller than the last, or when the nitrogen appears in a variable proportion at different stages of the analysis, then it is necessary to collect and measure the whole nitrogen evolved, which is not easily done with accuracy. To get rid of the nitrogen of the air contained in the tube, a

combustion tube is chosen 24 inches long, 6 inches of which at the closed end are filled with carbonate of copper, then follow 2 inches of pure oxide of copper, next the mixture of the substance with oxide of copper, then another layer of pure oxide, and lastly a layer of copper turnings. The air is exhausted from the tube by a syringe, and the tube filled with carbonic acid by heating one half of the carbonate of copper; the exhaustion and evolution of carbonic acid are several times repeated, till the whole air is certainly withdrawn from the tube, and the latter is filled with carbonic acid. The combustion of the mixture is then conducted as in the previous case, the gases however are received in a large graduated jar, over mercury, half full of a strong solution of caustic potash. After the combustion is completed, heat is again applied to the end of the tube containing the remaining half of the carbonate of copper, and carbonic acid evolved which sweeps out the last portions of nitrogen into the receiver, where the volume of that gas is observed.

MM. Will and Varrentrapp have lately proposed the following excellent method of determining the nitrogen in organic substances, which is likely to supersede every other. The substance is mingled with a mixture of caustic lime and hydrate of soda, and heated to redness in a combustion tube. All the nitrogen of the substance escapes as pure ammonia, which may be condensed in a small apparatus containing dilute hydrochloric acid. This liquid is afterwards mixed with chloride of platinum, and brought to dryness in a water-bath; the double chloride of platinum and ammonium remaining is washed with a mixture of alcohol and ether, in which it is perfectly insoluble. The quantity of nitrogen is calculated from the weight of the chloride of platinum and ammonium, or from the metallic platinum which it leaves behind when heated to redness.

Oxide of copper is not applicable for the combustion of substances containing chlorine, owing to the volatility of the chloride of copper, a portion of which passes into the chloride of calcium tube, and vitiates the determination of the hydrogen. Chromate of lead is then employed in the combustion tube, with the same manipulations as with oxide of copper. This salt must first be strongly ignited till it begins to melt and then be reduced to a very fine powder; the chloride of lead is

perfectly fixed at a low red heat. The chromate of lead is not in the slightest degree hygroscopic, and is likely to be preferred to oxide of copper, where it is desirable to determine the proportion of hydrogen with extreme accuracy.

Notwithstanding the great value of the analytical results of this method, and the agreement almost perfect in repetitions of the same analysis, there can be little doubt that the method itself is not absolutely exact. From the rigorous examination to which the combustion process has lately been submitted by M. Dumas, it appears to give less than the true quantity of carbon. The loss of carbon is ascribed to several causes: some is deposited here and there in the tubes and for want of oxygen not burned; the reduced copper is partly converted into carburet of copper; the liquid potash allows a portion of the carbonic acid to escape, and lastly the air which is drawn through the apparatus takes up some water from the same potash and diminishes its weight. This loss of carbon was hitherto concealed by carbonic acid being allowed to contain more carbon than it really has, so that the carbon lost in the process was made up in the calculation; and the formulæ deduced from analyses are only true from the accidental compensation of these two errors. Dumas reduces the proportion of carbon in carbonic acid from 27.67 to 27.27 per cent, and obtains for the atom of that element the number 75, instead of 76.4. This important result he has deduced by collecting and weighing the carbonic acid produced by the combustion of a known weight of pure charcoal, in the forms of graphite and the diamond.* Drs. Marchand and Erdman of Berlin have repeated these analyses with the same results; it is now indeed generally allowed that the atomic weight of carbon of Berzelius is too high, but chemists are not yet agreed as to the amount of reduction to be made. MM. Redtenbacher and Liebig conclude that the atomic weight of carbon is the intermediate number 75.854, from an elaborate series of experiments undertaken to determine the point, in which the proportion of silver in the acetate, malate, racemate and tartrate of that base was ascertained with great accuracy; the atomic weight of silver, respecting which there is little uncertainty, being taken at 1351.6. It has also been

* MM. Dumas and Stass, *Annales de Chimie et de Physique*, 3me. Série, tome 1, p. 5. (1841).

shewn by Dr. Clark that when certain corrections are made on the calculations of Berzelius' experiments, they really give a number for carbon nearly approaching to this.

To give the process of organic analysis all the precision of which it is susceptible, M. Dumas requires attention to the following circumstances. 1. To triple at least the quantity of matter usually employed. 2. After the ignition of the combustion tube to pass through it a large quantity of oxygen, so as to burn the deposited carbon and re-oxidate all the copper, which gets rid of the carburet of copper. 3. For the reception of the water to employ a chloride of calcium tube accompanied by a tube filled with fragments of pumice impregnated with oil of vitriol. 4. To absorb the carbonic acid, Liebig's bulb apparatus containing solution of potash is to be used, accompanied by tubes containing potash moistened with the potash ley on one side, and dry potash on the other; the dry potash arrests the water with which the gas has become charged by passing through the liquid in the bulbs.* The most important observation of Dumas is that the combustion of the carbon is never complete, unless oxygen be passed through the tube containing the mixture of oxide of copper and matter to be analysed, and the matter be thus burned in an atmosphere of oxygen. This is the principle of the method of organic analysis originally practised by Dr. Prout, by which he was led to the conclusion that the atom of carbon is exactly 6 on the hydrogen scale, or 75 on the oxygen scale.† M. Dumas, who now adopts this conclusion, has therefore been conducted to it by a recurrence to Dr. Prout's own mode of investigation.

MODIFICATIONS OF ORGANIC COMPOUNDS PRODUCED BY ARTIFICIAL PROCESSES.

It is generally stated that no substances properly organic can be produced by directly uniting their ultimate elements; although a few organic compounds may be formed from subs-

* *Annales de Chimie et de Physique*, 3me Série, tome 1, p. 39, where the improved process is minutely described and the apparatus figured.

† *Phil. Trans.* 1827; or *Brande's Manual of Chemistry*, p. 1060.

tances less complex than themselves, but which are not elementary; as urea from cyanic acid and ammonia, the acid named, in common with cyanogen itself and all its compounds, being considered organic, because usually derived from the decomposition of azotised matters. But it has unequivocally been proved that nitrogen gas unites with charcoal under the influence of carbonate of potash at a red heat, and forms cyanide of potassium (L. Thompson, Fownes).^{*} The last salt also yields ammonia when decomposed by water; so that cyanogen, and through cyanogen ammonia, can be primarily derived from their elements contained in the inorganic world. The usual course however pursued by the chemist in this department is to form new compounds by the alteration of compounds supplied to him by nature. These changes he effects by various agencies, such as hydrate of potash, distillation by heat, acids, oxygen, chlorine, &c. The most uniform and definite of these actions are those of a hydrated alkali and dry distillation.

Distillation with an alkali.—When an organic substance containing no nitrogen is fused with a sufficient quantity of hydrate of potash, no charcoal is liberated. The products formed are those which result from oxidation; water is generally decomposed, of which the oxygen enters into combination with the hydrogen and carbon of the organic matter, while the hydrogen is disengaged as gas. Thus when acetate of soda is decomposed by hydrate of barytes, the hydrogen of the latter is liberated. M. Dumas has shewn that alcohol and other bodies of the same character, distilled at a moderate heat with a mixture of hydrate of potash and quicklime, each gives rise to a peculiar acid, which remains in combination with the potash, by losing 2 eq. of hydrogen (disengaged as gas), and acquiring 2 eq. of oxygen; alcohol to acetic acid, wood spirit to formic acid, fousel oil to valerianic acid, ethal to ethalic acid; and that this mode of decomposition is characteristic of alcohols. Glycerine, which in some respects resembles an alcohol, when treated in the same way, but at a very low temperature, does not give a peculiar glyceric acid, but resolves itself into acetic and formic acids, with the loss of two equivalents of hydrogen and assumption of two of oxygen. Acetone transmitted in the state of

^{*} Originally observed by Desfosses; *Journal de Pharmacie*, t. 14, p. 280 (1828).

vapour over the mixture of hydrate of potash and lime heated to redness, gives nothing but carbonic acid, which remains in combination with the alkali, and light carburetted hydrogen C_2H_4 . The vapour of aldehyde passed over the same mixture at a lower temperature gives acetate of potash and free hydrogen, losing only one equivalent of hydrogen and acquiring one of oxygen, or the reaction is similar to what occurs with the next substance to be mentioned, to which aldehyde has considerable analogy.* Oil of bitter almonds distilled with dry hydrate of potash, gives hydrogen gas and benzoate of potash.

According to the temperature, ulmic, acetic and oxalic acids appear in other cases, or carbonic acid only. Thus tartaric acid fused with hydrate of potash gives the acetate and oxalate of potash. Acetate of potash distilled with a mixture of hydrates of potash and lime, gives carbonate of potash and light carburetted hydrogen gas, which on that account is also named the gas of the acetates. Formic acid, alcohol, and bodies in general consisting of carbon, oxygen and hydrogen, when distilled with anhydrous barytes, give the same gas. When substances containing nitrogen are boiled in a solution of caustic potash, or fused with the dry hydrate, ammonia is evolved, and acids containing no nitrogen remain in combination with the potash. Some bodies containing much nitrogen lose only, with dry hydrate of potash, a portion of their nitrogen in the form of ammonia; and the rest acquiring oxygen, assumes the form of cyanic acid, and is protected by the potash from farther decomposition.

When the acetate of any metallic oxide capable of retaining carbonic acid at a red heat, such as the acetate of soda, potash, barytes, &c., is distilled, a carbonate remains in the retort, while a combustible liquid, acetone C_3H_3O distils over. M. Fremy has shewn that sugar, starch and all those ternary compounds of carbon, hydrogen and oxygen, in which the two last are in the proportion to form water, are decomposed when heated in contact with lime in the same manner as acetic acid. They afford acetone, with water and carbonic acid. Benzoic acid distilled with three times its weight of hydrate of lime forms carbonate of lime, with a volatile liquid $C_{12}H_6$.

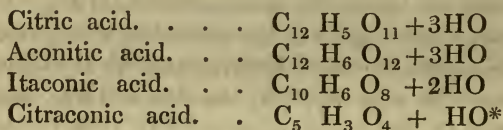
* Annales de Chimie et de Physique, tome 73, p. 113.

the benzin of Mitscherlich and bicarburet of hydrogen of Faraday. The neutral benzoate of lime gives with other products the liquid benzone, $C_{13}H_5O$. Distilled from lime stearic, margaric and oleic acids lose the elements of carbonic acid, and form neutral volatile products, stearone, margarone and oleone. The names of such pyrogen bodies terminate in *one* as contain one atom of oxygen and are neutral. Margarone carried in its turn over lime at a red heat, loses its oxygen, in the form of carbonic acid, and paraffin is produced, which is a binary compound of carbon and hydrogen. Thus the alkali determines throughout the formation of a highly oxidised acid body, with which it unites and the other products are consequently partially or completely deoxidised.

Dry distillation.—Many organic substances are volatile and may be distilled at a moderate heat without alteration, such as alcohol and most essential oils; but a larger number are fixed. The latter when submitted alone to distillation usually abandon carbon, and form new and more simple volatile products. Three periods are distinguished by Liebig in the dry distillation of the fixed organic acids, from the different compounds formed according to the temperature. In the first, organic acids of less atomic weight are produced, with carbonic acid, water and inflammable liquids soluble in water. The bibasic and tribasic organic acids, by losing the elements of water and carbonic acid, are converted into their volatile pyr-acids, which are less basic, generally monobasic; thus tartaric acid $C_8H_4O_{10}$ is converted into pyrotartaric acid $C_5H_3O_3$, by losing three atoms of carbonic acid C_3O_6 and one atom of water HO ; but these pyr-acids can rarely be distilled again by themselves, without partial decomposition. In the second period of the distillation, bodies are obtained which result from the destruction of the preceding compounds; thus the oxygen of the acids, uniting with the carbon and hydrogen of the combustible bodies, gives rise to more simple bodies, such as carbonic oxide, carbonic acid and water; some charcoal is generally set at liberty, while another portion of it enters into combination with the excess of hydrogen, and produces liquid or solid volatile hydrocarbons. In the last period, nothing is obtained but charcoal and a gaseous mixture, principally composed of carbonic acid, carbonic oxide, olefant gas and light carburetted hydrogen. Substances con-

taining nitrogen, give ammonia in the first period, and cyanogen or hydrocyanic acid in the last.

The decomposition of citric acid by heat, has been more minutely investigated than any other, by M. Crasso, and is particularly interesting from the variety of products it affords, at different stages of the decomposition. After losing its water of crystallization, the citric acid, $C_{12}H_5O_{11}$, first undergoes a decomposition, of which the products are a new and fixed acid, aconitic acid, $C_4H_2O_4$, also found in nature being the acid of the *aconitum napellus*, together with one atom of acetone C_3H_3O , four atoms of carbonic oxide C_4O_4 , and one atom of carbonic acid CO_2 . By a continuance of the heat, the fixed aconitic acid itself is decomposed, three atoms of it $C_{12}H_6O_{12}$, affording two atoms of a volatile pyr-acid, named itaconic acid $2(C_5H_3O_4)$, and two atoms of carbonic acid C_2O_4 . The itaconic acid again is decomposed when heated to its point of ebullition, and gives a more volatile and stable acid, named citraconic acid $C_5H_3O_4$, which is consequently isomeric with the preceding acid. It is believed, however, by Crasso, that the last is the only monobasic acid in the series, and that the true formulæ of the hydrates of the three new acids produced by the decomposition of citric acid by heat, are, with that of the original acid itself :



By the united action of heat and bases, other transformations of acids have been effected. Thus malic acid is converted into fumaric and equisetic acids, and citric acid into aconitic and tartaric acids, when their compounds with oxide of antimony or potash are heated so long as water is disengaged.

ACTION OF OXYGEN—EREMACUSIS.

Organic compounds when dry and in a state of purity are generally capable of resisting the action of the air or of free oxygen, at the usual temperature ; but a considerable

* Annales de Chimie et de Physique, 3me Série, tome 1, p. 311.

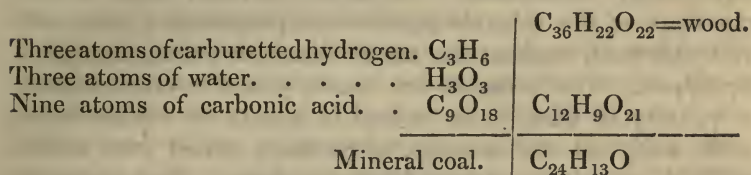
number are affected by that element; the various essential and fixed oils absorb oxygen in different degrees, the first becoming resins and the second acquiring the drying properties of varnishes; the essential oil of bitter almonds is gradually converted into benzoic acid, and the vapour of ether passes slowly into acetic acid, while white indigo and other colouring principles undergo remarkable changes from a rapid absorption of oxygen. The direct oxidation of alcohol and ether, which gives rise to acetic acid, is greatly favoured by the contact of spongy platinum. The highly oxygenised acids act with much more energy upon organic compounds and give rise to various products according to the quantity of oxygen communicated. Thus alcohol is converted by oxidating matters, into acetal, aldehyde, acetic acid, formic acid, oxalic acid, carbonic acid and water. In these reactions, the oxygen is frequently observed to affect the hydrogen exclusively, which is converted into water, while a quantity of oxygen exactly equivalent to the hydrogen thus withdrawn, enters into combination with the remaining elements, and appears to be substituted for the hydrogen. Thus by the action of four atoms of oxygen, upon one atom of alcohol $C_4H_5O + HO$, two atoms of hydrogen are withdrawn as water, while two atoms of oxygen are at the same time absorbed by the remaining elements of the alcohol, which becomes hydrated acetic acid $C_4H_3O_3 + HO$. When anhydrous sugar $C_{12}H_9O_9$ is treated with hypermanganate of potash, the nine atoms of hydrogen which the former contains are replaced by nine atoms of oxygen, and six atoms of oxalic acid formed $6C_2O_3$.

The presence of water greatly promotes the action of the oxygen of the atmosphere upon organic substances. The name *eremacausis* has been applied by Liebig to the slow combustion or oxidation of organic matters in air. Vegetable juices evaporated by a gentle heat in air allow a brown or brownish black substance to precipitate, known as *extractive matter*, and similar in properties from whatever juice it is formed. It is insoluble or very sparingly soluble in water, but dissolved with facility by alkalies. By the action of air upon solid animal or vegetable matters, a similar pulverulent brown substance is formed known as *humus*. According to an observation of De Saussure, the sawdust of oak wood converts oxygen into carbonic acid, without

any change of the volume of the gas; but while dry sawdust lost three parts by weight of carbon in this way, it diminished in weight by fifteen parts altogether, shewing that twelve parts of water were at the same time separated from the wood. Hence the proportion of carbon in decaying wood increases with the progress of its decay; and it is concluded that the hydrogen only is oxidised at the expense of the oxygen of the air, while the carbonic acid is formed from the elements of the wood (Liebig). The composition of pure woody fibre or lignin being $C_{36}H_{22}O_{22}$, two different specimens of mouldered oak wood, (the humus from oak wood) were found to be $C_{35}H_{20}O_{20}$ and $C_{34}H_{18}O_{18}$, or for every two atoms of hydrogen oxidised by the air, one atom of carbonic acid (CO_2) has been formed at the same time from the elements of the wood and set free. When water is present and the access of air restrained, the decomposition of wood appears to proceed in a different manner; for while carbonic acid is generated as before, a certain quantity of water enters into chemical combination, white mouldering beechwood being found to have a composition corresponding with the formula $C_{33}H_{25}O_{24}$. There is reason, however, to suppose the interference in such cases of mouldering, of a species of fermentation such as was observed when rags were placed in heaps and wetted in the preparation of a substance for the fabrication of paper, according to the old process in use before the application of chlorine. The rags became warm and disengaged a gas, while their weight diminished from 18 to 25 per cent. It is probable that in this, as well as other putrefactive processes, the oxygen of the water assists in the formation of carbonic acid.

Wood coal or brown coal, which retains the structure of the wood unchanged, appears to be produced by a similar process of decomposition. A specimen free from bituminous matter was found to have a composition expressed by the formula $C_{33}H_{21}O_{16}$; and may therefore have been produced from woody fibre by the separation of one equivalent of hydrogen and three equivalents of carbonic acid. In all varieties of wood coal, the proportion of oxygen in relation to the hydrogen is diminished, these elements existing in the original woody fibre in the same proportion as in water, indicating a disengagement of carbonic acid from their substance, which appears still to go

on at great depths in all the strata of wood coal. The composition of the splint coal of Newcastle and cannel coal of Lancashire being $C_{24}H_{13}O$, according to the analyses of both Richardson and Regnault, mineral coal is obviously formed from woody fibre in a different manner from brown coal. The composition of both splint and cannel coal is obtained by the subtraction of 3 atoms of carburetted hydrogen, 3 atoms of water, and 9 atoms of carbonic acid from the formula of wood (Liebig):



Caking coal from Caresfield, near Newcastle, is $C_{20}H_9O$, or contains the elements of cannel coal, *minus* the constituents of olefiant gas C_4H_4 (Liebig). The inflammable gas of coal mines is principally light carburetted hydrogen, but it has been observed by Bischoff occasionally accompanied by notable quantities of olefiant gas. Such decompositions, however, are not due to eremacausis, and indeed take place in materials covered by such a mass of strata as must entirely exclude air, but are more analogous to the internal reactions observed in organic matters, and known as species of fermentation, in which the elements of a compound substance (such as sugar) divide themselves into two or more groups, without the incorporation of any extraneous element, except perhaps the constituents of water.

The absorption of oxygen by alcohol in its acetification is a true eremacausis, so also is the process of nitrification. Oxidation is promoted in many organic bodies by contact with an alkali; thus alcohol holding potash in solution soon becomes brown from oxidation, and a resinous matter appears with all the products of the decomposition of aldehyde. The oxidation of gallic acid, hematin and many other compounds is promoted by the same influence; many vegetable substances exhibit a rapid absorption of oxygen on the addition to them of ammonia, and form splendid violet or red coloured liquids, such as the colouring principles of the lichens. On the other hand,

eremacausis seems to be entirely prevented when water is excluded, or when the substance is exposed to a temperature of 32° . The processes of fermentation and putrefaction, which are different from eremacausis, appear to be necessarily preceded by an absorption of oxygen. Thus the juice of grapes pressed under mercury and collected in a jar filled with that metal was observed by Gay-Lussac to keep without change, but on admitting a bubble of air to the liquid, the vinous fermentation immediately commenced. The perfect exclusion of air is also the basis of the valuable process for preserving animal and vegetable food, without the use of antiseptics, first introduced by Appert. The materials are usually placed in canisters with a quantity of fluid, which is kept in a state of ebullition for some time, and the openings hermetically closed with solder while the vessels are entirely filled with steam. Eremacausis is also prevented or much retarded by aromatic substances, empyreumatic substances and oil of turpentine, the vapours of which retard the oxidation of phosphorus and of phosphuretted hydrogen in a similar manner. It is also arrested by mineral acids and salts of mercury, which appear to act by combining with the organic matter; alcohol, a strong solution of sugar, common salt and many other saline substances are supposed to owe their antiseptic properties in a great measure to their affinity for water, which reduces animal or vegetable matters in contact with them to a state of dryness in which they are little liable to decomposition. Thus a piece of dry butcher-meat covered with dry salt is found after twenty-four hours swimming in brine, the salt attracting water from the meat, and leaving it not humid enough for chemical action.

ACTION OF CHLORINE, ITS SUBSTITUTION FOR HYDROGEN,
CHEMICAL TYPES.

M. Gay-Lussac observed, several years ago, that bees' wax exposed to chlorine gas absorbed the latter, giving rise to a disengagement of hydrochloric acid, without any change of volume in the gas from the operation. The reason is that the wax loses a volume of hydrogen equal to the volume of chlorine which it absorbs, the constituents of hydrochloric acid gas being united, it is to be remembered, without any condensation of

volume. M. Dumas afterwards repeated the experiment with oil of turpentine, and obtained a similar result; 4H in the latter body being replaced by 4Cl, or $C_{20}H_{16}$ becoming $C_{20}H_{12}Cl_4$. The action of chlorine on a great number of organic substances has since been observed by MM. Dumas, Laurent, Regnault, Malaguti and others, and found to be remarkably uniform. The investigation has led to the formation of a large number of new compounds, and to the propagation of certain theoretical views by M. Dumas, which have had an extraordinary influence on the recent progress of organic chemistry.

When light carburetted hydrogen gas C_2H_4 , is allowed to mix gradually with three times its volume of chlorine, in strong sunshine, the whole 4 eq. of hydrogen are converted into hydrochloric acid, which is liberated, while the 2 eq. of carbon combine with 4 eq. of chlorine, and form a peculiar liquid chloride of carbon C_2Cl_4 ; so that the hydrogen of the former compound appears to be simply replaced by chlorine in the latter.* The removal of the whole hydrogen by chlorine takes place at once, in this hydrocarburet without the formation of any other intermediate product except a trace of chloroform, but in other cases, where there are several equivalents of hydrogen, the latter are often removed and replaced by chlorine one by one, and a series of bodies formed in which while the hydrogen diminishes, the chlorine increases in an equal proportion; such are the compounds produced by the action of chlorine on Dutch liquid already described (page 375), and the remarkable series produced by the repeated action of chlorine upon hydrochloric ether.† The two series referred to, exhibit a remarkable isomerism, the corresponding products having the same composition although distinguishable by their physical properties and by the effect of re-agents upon them. These chlorine compounds are all volatile liquids, with the exception of the solid perchloride of carbon which is common to both series.

* Dumas, *An. de Ch. et de Ph.* t. 73, p. 94.

† Regnault, *An. de Ch. et de Ph.* t. 71, p. 353.

OLEFIANT GAS AND BODIES DERIVED FROM IT BY THE
ACTION OF CHLORINE.

Olefiant gas	$C_4H_3 + H$
First product, Dutch liquid	$C_4H_3Cl + HCl$
Second product	$C_4H_2Cl_2 + HCl$
Third product	$C_4HCl_3 + HCl$
Last product, perchloride of carbon	C_4Cl_6

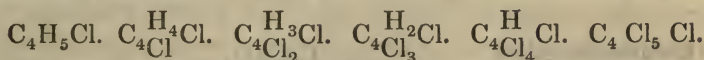
HYDROCHLORIC ETHER (CHLORIDE OF ETHYL) AND BODIES
DERIVED FROM IT BY THE ACTION OF CHLORINE.

Hydrochloric ether	C_4H_5Cl
Monochlorinated ditto	$C_4H_4Cl_2$
Bichlorinated ditto	$C_4H_3Cl_3$
Trichlorinated ditto	$C_4H_2Cl_4$
Quadrichlorinated ditto	C_4HCl_5
Perchloride of carbon	C_4Cl_6

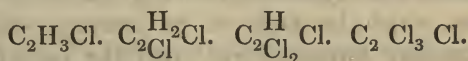
It appears from the second table that hydrochloric ether is affected at once by two atoms of chlorine, one of which seizes an atom of hydrogen and removes it in the form of hydrochloric acid, while the second atom of chlorine enters into the compound remaining, which Regnault distinguishes as monochlorinated hydrochloric ether, the name having reference to the mode of derivation of the compound and not its composition.* The latter body when exposed to chlorine is likewise affected by two atoms, one of which seizes and withdraws an atom of hydrogen, while the other unites with the remaining elements, forming bichlorinated hydrochloric ether. The trichlorinated and quadrichlorinated compounds, and the perchloride of carbon, which follow, have the same mode of formation; and as one atom of chlorine is communicated for each atom of hydrogen withdrawn, the entire number of constituent atoms remains the same, or ten, throughout the series, and the last member differs only from the first, in having 5 atoms of chlorine instead of 5 of hydrogen. To exhibit the complimentary function of

* "Chlorinated" appears to be a preferable term to *chloruretted*, to apply to such a compound, as the last is already used in a different sense.

the chlorine and hydrogen in these bodies, their formulæ may be written thus :



Chloromethylic ether or chloride of methyl $\text{C}_2\text{H}_3\text{Cl}$, a body having the same relation to wood-spirit that hydrochloric ether has to alcohol, gives rise to an analogous series of chlorinated compounds when a stream of chlorine is passed through it, the product being treated in its turn with the gas, and the same process repeated with the new product ; when the hydrogen is then entirely withdrawn, and a chloride of carbon remains, the same that is derived from light carburetted hydrogen (Regnault). The bodies of this series are :—



All these chlorinated compounds possess the neutral character of the bodies from which they are derived. Malaguti has also observed that ether (oxide of ethyl) may lose two equivalents of hydrogen and gain two of chlorine, $\text{C}_4\text{H}_5\text{O}$ becoming $\text{C}_4\text{H}_3\text{Cl}_2\text{O}$, without any of its essential properties undergoing alteration ; for its power of combination remains the same, and chlorinated ether is still ether. Oxalic ether or the oxalate of oxide of ethyl, may have its whole five atoms of hydrogen replaced by five atoms of chlorine, and chlorinated oxalic ether, or chloroxalic ether is formed ; $\text{C}_4\text{H}_5\text{O} + \text{C}_2\text{O}_3$ becomes $\text{C}_4\text{Cl}_5\text{O} + \text{C}_2\text{O}_3$, or adopting empirical formulæ, $\text{C}_6\text{H}_5\text{O}_4$ becomes $\text{C}_6\text{Cl}_5\text{O}_4$. Now each of these ethers is the base of a class of salts, the oxalovينات and chloroxalovينات ; each of them, also, is affected by dry ammoniacal gas, and by solution of ammonia in the same way, forming oxamethane or chloroxamethane with the first re-agent, and oxamide with the second :*

OXALIC ETHER, AND COMPOUNDS DERIVED FROM IT.

Oxalic ether	. . .	$\text{C}_6\text{H}_5\text{O}_4$
Oxalovinic acid (hydrated)		$\text{C}_6\text{H}_5\text{O}_4 + \text{C}_2\text{O}_3, \text{HO}$
Oxamethane	. . .	$\text{C}_6\text{H}_5\text{O}_4 + \text{C}_2\text{O}_2, \text{NH}_2$
Oxamide	. . .	$\text{C}_2\text{O}_2, \text{NH}_2$

* Malaguti, Annales de Chimie, etc. t. 74, p. 299.

CHLOROXALIC ETHER, AND COMPOUNDS DERIVED FROM IT.

Chloroxalic ether	. . .	$C_6Cl_5O_4$
Chloroxalovinic acid (hydrated)		$C_6Cl_5O_4 + C_2O_3, HO$
Chloroxamethane	. . .	$C_6Cl_5O_4 + C_2O_2, NH_2$
Oxamide	. . .	$C_2O_2, NH_2.$

It rarely happens that the crystalline forms of corresponding hydrogen and chlorine compounds can be compared, for most frequently the two substances, or at least one of them, does not crystallize, and is altogether incapable of exact measurement. But M. de la Provostaye has succeeded in instituting a comparison between the crystalline forms of oxamethane and chloroxamethane, which he finds to be isomorphous, or rather different secondary forms derived from the same fundamental form.* This would establish the isomorphism of chlorine and hydrogen, but it is to be regretted that so important a conclusion should rest upon a single instance, and one also in which, as Mitscherlich remarks, the usual complete identity of form of isomorphous bodies is not observed.

By exposing pure acetic acid to the action of dry gaseous chlorine, under the direct influence of the solar rays, M. Dumas has replaced the whole hydrogen of that acid by chlorine, or converted acetic acid $C_4H_3O_3 + HO$ into chloracetic acid $C_4Cl_3O_3 + HO$, without altering the capacity of saturation of the acid, or its combining measure in the state of vapour.† Decomposed by alkalies, these two acids give likewise analogous products, acetic acid yielding carbonic acid C_2O_4 with light carburetted hydrogen, C_2H_4 , and chloracetic acid yielding carbonic acid C_2O_4 with chloroform C_2HCl_3 ; the body last mentioned being viewed as carburetted hydrogen in which three atoms of hydrogen are replaced by three of chlorine.

Many similar cases of the substitution of chlorine for hydrogen have been observed, but those already adduced are sufficient to illustrate the mode of replacement, and to prove that a

* Philosophical Magazine, 3rd Series, vol. 18, p. 372.

† Annales de Chimie et de Physique, tome 73, p. 77.

compound may preserve its leading chemical characters, although its hydrogen be exchanged for chlorine. Chemists were not prepared for the admission of this equivalency of chlorine and hydrogen from anything observed in inorganic compounds. The two elements seemed, indeed, to be strongly contrasted, chlorine typifying the electro-negative or salt-radical class of elements, and hydrogen belonging, incontestably, to the electro-positive or basyle class with the metals, although not occupying a high place in that class. One equivalent of chlorine being also isomorphous with *two* equivalents of manganese, to which latter element hydrogen appeared to be related, as a member of the magnesian family, the isomorphous relation to be looked for was one of chlorine with two of hydrogen, and not with one of hydrogen as in oxamethane and chloroxamethane lately commented upon.

But it is to be remembered that no body is absolutely chlorous (electro-negative), or zincous (electro-positive), but only relatively so to certain other bodies. Hence although zincous to chlorine, hydrogen is chlorous to carbon, or *hydrogen is the chlorous constituent of the organic compounds in question*. Even among inorganic compounds, we have instances of hydrogen discharging the same function, as in the class of phosphuretted hydrogen and arseniетted hydrogen, where 3 atoms of hydrogen are chlorous, and may be replaced by oxygen, chlorine, etc. (In ammonia, on the contrary, nitrogen appears to be the negative, and hydrogen the positive constituent.) In this way that universal dualism in the constitution of a compound, or distribution of its elements into two opposed classes, conducing to binary combination, which has never ceased to be a recognised doctrine of chemical science, in some form or other, with reference to inorganic compounds, is extended also to organic compounds. Such a doctrine which might always have been maintained on abstract grounds appears now to be inevitable from the observed substitutions of chlorine for hydrogen. Hydrogen then being viewed as a chlorous element in such compounds as carburetted hydrogen and olefiant gas, while carbon is the basyle or zincous element, the former element may therefore be replaced by other bodies higher than itself in the scale of salt-radicals, such as chlorine, without any essential derangement of the constitution

of the original compound. The equivalent substitution of chlorine for hydrogen is thus admitted in its full extent. This substitution appears to confirm and extend what is generally understood at the electro-chemical distribution of elements, on which our ideas of binary combination are founded, and not to be opposed to or incompatible with such views.

The isomorphism of chlorine and hydrogen, equivalent for equivalent, if confirmed, will cause the removal of the latter element from the magnesian class, but establishes a relation between hydrogen and silver, and therefore places the former on the verge of the potassium group. Hydrogen certainly possesses many relations to mercury, if not absolutely isomorphous with that metal (page 656).

By a *chemical type* M. Dumas understands a certain number of elements combined together, every one of which, whatever be its nature, may be replaced by another, and indeed every one in its turn, so that not a trace of the original compound may remain. The arrangement of the elements in regard to each other remains always the same, and that is the character of the type. Thus all the chlorinated compounds derived from hydrochloric ether, including perchloride of carbon, contain ten atoms, which are supposed to have the same arrangement as in hydrochloric ether itself. Aldehyde produced by the partial oxidation of alcohol, and chloral by the action of chlorine upon alcohol, contain the same number of atoms and belong to one type:

Aldehyde, $C_4H_3O + HO$, or $C_4H_4O_2$.

Chloral, $C_4Cl_3O + HO$, or $C_4\overset{Cl}{H}O_2$.

When on the other hand, an atom is withdrawn from a compound without being replaced by another, the atoms which remain cannot retain their original position, and a new type must result. It is supposed by Dumas, that chlorine may replace carbon, nitrogen and other elements besides hydrogen, and any one element, indeed any other, without destruction of the primitive type. Such substitutions however, have not been effected, and on the view of substitution taken above are not to be expected, for carbon at least must always be considered as the basyle or electro-positive constituent of organic com-

pounds, and never like oxygen, nitrogen and hydrogen, as chlorous or electro-negative. Even where chlorine replaces hydrogen, the type is not uniformly preserved, for we find occasionally the same body derived by substitution from two different types, as perchloride of carbon from both Dutch liquid and hydrochloric ether.

The reference of bodies to a common type has often an advantage over their classification under a common radical or according to any theory of constitution, as it involves less that is speculative. The former asserts only that the bodies contain the same number of atoms and have a common constitution, but says nothing as to what that constitution is. Hence a type may be denoted by an empirical formula of the simplest kind expressing nothing but the elements and their number, in which changes by substitution can be distinctly exhibited. It is useful, in the present uncertain state of our knowledge respecting the constitution of organic compounds, to have such a mode of expressing compounds and exhibiting their relations in composition, but it does not supersede rational theories of constitution.

TRANSFORMATIONS OF ORGANIC SUBSTANCES.

ACTION OF FERMENTS.

Complex organic substances frequently divide themselves into two or more compounds of a simpler constitution, without the intervention of any intelligible chemical agency. The presence of a second organic substance, however, is an essential condition of such transformations, although the latter substance does not contribute to the change by imparting any new element to the decomposing body, nor by abstracting any element from it. The resolution of sugar into carbonic acid and alcohol in fermentation, by the contact of yeast, is a familiar example of such a change (page 760). Decomposition of this kind has been distinguished as *catalysis*, and the second body which determines the changes in the first, by an action of presence, termed the *catalytic agent* (page 195). The recent study of such decompositions has revealed the circumstance that the activity of the catalytic agent is connected with its being itself

in a state of decomposition at the time. The yeast is only active when, by access of air, it has become subject to oxidation, and the decomposition of the sugar is looked upon by M. Liebig as a reflex action of the decomposition of the yeast. The views of that eminent philosopher on the action of yeast and other ferments will be best explained in his own words.

“This action may be expressed by the following law, long since proposed by Laplace and Berthollet, although its truth with respect to chemical phenomena has only lately been proved. ‘A molecule set in motion by any power can impart its own motion to another molecule with which it may be in contact.’”

This is a law of dynamics, the operation of which is manifest in all cases, in which the resistance (force, affinity, or cohesion,) opposed to the motion is not sufficient to overcome it.

We have seen that ferment or yeast is a body in the state of decomposition, the atoms of which, consequently, are in a state of motion or transposition. Yeast placed in contact with sugar, communicates to the elements of that compound the same state, in consequence of which, the constituents of the sugar arrange themselves into new and simpler forms, namely, into alcohol and carbonic acid. In these new compounds the elements are united together by stronger affinities than they were in the sugar, and therefore under the conditions in which they were produced further decomposition is arrested.

We know, also, that the elements of sugar assume totally different arrangements, when the substances which excite their transposition are in a different state of decomposition from the yeast just mentioned. Thus, when sugar is acted on by rennet or putrefying vegetable juices, it is not converted into alcohol and carbonic acid, but into lactic acid, mannite, and gum.

Again, it has been shown, that yeast added to a solution of pure sugar gradually disappears, but that when added to vegetable juices which contain gluten as well as sugar, it is reproduced by the decomposition of the former substance.

The yeast with which these liquids are made to ferment, has itself been originally produced from gluten.

The conversion of gluten into yeast in these vegetable juices is dependent on the decomposition (fermentation) of sugar; for, when the sugar has completely disappeared, any gluten which

may still remain in the liquid, does not suffer change from contact with the newly-deposited yeast, but retains all the characters of gluten.

Yeast is a product of the decomposition of gluten; but it passes into a second stage of decomposition when in contact with water. On account of its being in this state of further change, yeast excites fermentation in a fresh solution of sugar, and if this second saccharine fluid should contain gluten, (should it be *wort*, for example,) yeast is again generated in consequence of the transposition of the elements of the sugar exciting a similar change in this gluten.

After this explanation, the idea that yeast reproduces itself as seeds reproduce seeds, cannot for a moment be entertained”.*

To these may be added the results of the very recent inquiries of MM. Boutron and Fremy on the phenomena of the fermentation of malt. These chemists find that the same azotised matter in the grain, which acts as the ferment, passes through a succession of changes, and can excite different kinds of fermentation at different stages in the progress of its decomposition; that it is not one but a series of ferments. It is as diastase that it first appears, or this is the first condition of the ferment in the infusion of malt, as is proved by the action which it exerts upon starch, the latter being converted into sugar. From the acidity of the liquor which is afterwards observed, it is evident that the azotised matter next takes the character of the lactic ferment (page 808), and converts the sugar, to a certain extent, into lactic acid. A period then arrives at which the liquid, still transparent, becomes turbid, and the resulting precipitate is the matter which can produce the alcoholic fermentation; and it is only at this epoch that alcohol is formed and carbonic acid disengaged. That it is the insoluble precipitate to which the alcoholic fermentation should be ascribed, is proved by filtering the liquid to separate the ferment, when the alcoholic fermentation is immediately arrested.†

The action of yeast and all other ferments is destroyed by the

* Liebig's Organic Chemistry in its applications to Agriculture and Physiology, edited by Dr. Lyon Playfair.

† Ann. de Chim. &c. 3 serie, t. 2, p. 269.

temperature at which water boils, by alcohol, by acids, salts of mercury, sulphurous acid, chlorine, iodine, bromine, by aromatic substances, volatile oils, and particularly empyreumatic oils, smoke and a decoction of coffee, these bodies in some cases combining with the ferments or otherwise effecting their decomposition.

The following are additional instances of fermentation. The smell and taste which distinguish wine from all other fermented liquids depend upon *ænanthic ether*, which contains a peculiar acid; and those of spirits from corn or potatoes upon a peculiar oil, the *oil of potatoes*. Both of these substances are produced in fermentation, the former probably from the tartaric acid of the wine, the latter by a simultaneous decomposition of the cellular tissue of the grain or potato. The oil of potatoes has all the characters of an alcohol (page 813). The production of this oil is completely prevented in the fermentation of beer, by the presence of an aromatic substance, the volatile oil of hops. In the fermentation of the *Herba centaurium minorius*, a plant which possesses no smell, a true ethereal oil is formed, of a penetrating agreeable odour. The leaves of tobacco, when fresh, have little or no smell, and when distilled, yield a white, fatty, crystallizable substance (nicotianine), which contains no nitrogen and is quite destitute of smell. But when the same plant, after being dried, is moistened with water, tied together in small bundles, and placed in heaps, a peculiar process of decomposition takes place. Fermentation commences, and is accompanied by the absorption of oxygen; the leaves now become warm and emit the characteristic smell of prepared tobacco and snuff. When the fermentation is carefully promoted, and too high a heat avoided, this smell increases and becomes more delicate; and after the fermentation is completed, an oily azotised volatile matter, called *nicotine*, is found in the leaves. This substance which possesses all the properties of a base, was not present before the fermentation. The different kinds of tobacco are distinguished from one another, like wines, by having very different odoriferous substances, which are generated along with the nicotine (Liebig).

M. Liebig also ascribes the morbid action of matters of contagion and miasms, to their operation as ferments. He applies the law already quoted to organic substances forming part of

the animal organism. " We know that all the constituents of these substances are formed from the blood, and that the blood by its nature and constitution is one of the most complex of all existing matters.

Nature has adapted the blood for the reproduction of every individual part of the organism; its principal character consists in its component parts being subordinate to every attraction. These are in a perpetual state of change or transformation, which is effected in the most various ways through the influence of the different organs.

The individual organs, such as the stomach, cause all the organic substances conveyed to them which are capable of transformation to assume new forms. The stomach compels the elements of these substances to unite into a compound fitted for the formation of the blood. But the blood possesses no power of causing transformations; on the contrary, its principal character consists in its readily suffering transformations; and no other matter can be compared in this respect with it.

Now it is a well-known fact, that when blood, cerebral substance, gall, pus, and other substances in a state of putrefaction, are laid upon fresh wounds; vomiting, debility, and at length death, are occasioned. It is also well known that bodies in anatomical rooms frequently pass into a state of decomposition which is capable of imparting itself to the living body, the smallest cut with a knife which has been used in their dissection producing in these cases dangerous consequences.

The poison of bad sausages belongs to this class of noxious substances. Several hundred cases are known in which death has occurred from the use of this kind of food. In Wirtemberg especially, these cases are very frequent, for there the sausages are prepared from very various materials. Blood, liver, bacon, brains, milk, meal and bread, are mixed together with salt and spices; the mixture is then put into bladders or intestines, and after being boiled is smoked. When these sausages are well prepared, they may be preserved for months, and furnish a nourishing savoury food; but when the spices and salt are deficient, and particularly when they are smoked too late or not sufficiently, they undergo a peculiar kind of putrefaction which begins at the centre of the sausage. Without any appreciable escape of gas taking place, they become paler in colour, and

more soft and greasy in those parts which have undergone putrefaction, and they are found to contain free lactic acid or lactate of ammonia; products which are universally formed during the putrefaction of animal and vegetable matters.

The death which is the consequence of poisoning by putrefied sausages succeeds very lingering and remarkable symptoms. There is a gradual wasting of muscular fibre, and of all the constituents of the body similarly composed.

Sausages, in the state here described, exercise an action upon the organism, in consequence of the stomach and other parts with which they come in contact not having the power to arrest their decomposition; and entering the blood in some way or other, while still possessing their whole power, they impart their peculiar action to the constituents of that fluid.

MOLECULAR THEORY OF ORGANIC COMPOUNDS.

It is observed by Liebig that in all organic compounds it is necessary to consider two kinds of attraction, that of the contained radicals, and that of the ultimate elements themselves for each other; which last attraction is not superseded by the former. To these elemental attractions we are to look for an explanation of the phenomena of substitution.

Any theory of combination would be incomplete which did not provide in the constitution assigned to both elementary and compound bodies, for that propagation of chemical action to a distance which is witnessed in the voltaic circle. The consideration of that action has already forced upon us the conclusion that even a free element such as a metal, in the state in which we operate with it, has a complex molecular structure, its atoms being grouped, so as to represent binary compounds. Hence in combining two different elements, we have really to undo a previous but weaker combination in both cases, before the dissimilar elements unite; and consequently, even where combination appeared most direct, we have the compound really formed by a mutual double decomposition, or by the substitution of one element for another in pre-existing frames of compounds. The universal susceptibility of compounds of all kinds to decomposition under electrical action of high intensity,

appears also to argue a greater simplicity and sameness of constitution of chemical compounds than is generally recognised.

We are repelled by the idea of atoms of the same kind having the relation to each other of combination, for diversity of nature appears to be the reason why bodies combine. The intensity of the combination certainly increases with the diversity, but this does not prove that such diversity is an essential condition of combination. Combination, indeed, appears to be the natural condition of matter, the source of its cohesion and aggregation, which it retains by inertia, and decomposition to require the application of a force, such as the communication of heat to atoms which supplies them with the repulsive power required to overcome their combination.

The fundamental elemental combination of every compound is assumed to be binary, one element being chlorous (negative), and the other zincous or basic (positive); or one set of the elements being chlorous, and another set basic. This difference in the character of the elements of a compound may be expressed by writing its formula in two lines, placing the basic or positive elements in the lower, and the chlorous or salt-radical elements in the upper line:

Water $\frac{\text{O}}{\text{H}}$, carbonic acid $\frac{\text{O}_2}{\text{C}}$, hydrate of potash $\frac{\text{O.O}}{\text{K.H}}$, carbonate of potash $\frac{\text{O}_2.\text{O}}{\text{C.K}}$, olefiant gas $\frac{\text{H}_4}{\text{C}_4}$, or $\frac{\text{H}_2.\text{H}_2}{\text{C}_2.\text{C}_2}$; ether $\frac{\text{H}_5\text{O}}{\text{C}_4}$, alcohol $\frac{\text{H}_5\text{O.O}}{\text{C}_4.\text{H}}$.

Most of these formulæ are meant only to express that certain elements collectively are chlorous and certain others collectively basic. In ether, for instance, 4 atoms (C_4) are basic, against 6 atoms (H_5O) chlorous; but it is to be supposed that many compounds admit of a division into more simple binary compounds, olefiant gas $\frac{\text{H}_4}{\text{C}_4}$ into two binary compounds

$2\text{C}_2\text{H}_2$, expressed thus, $\frac{\text{H}_2.\text{H}_2}{\text{C}_2.\text{C}_2}$; or even four binary compounds

4CH , expressed thus, $\frac{\text{H.H.H.H}}{\text{C.C.C.C}}$. No particular binary arrangement of this kind, however, is at present insisted upon, unless in a few cases. All that is assumed is:

1. That the basic or positive element or elements are in immediate combination with the chlorous element or elements placed above them in the formulæ.

2. That these binary compounds again are *associated together* so as to form the compound molecule, from an attraction of all the basic elements for each other, and of all the chlorous elements for each other, of such a nature as retains together the 3 atoms of the same kind which form a single equivalent of nitrogen or phosphorus, the 3 atoms of cyanogen in cyanuric acid, the various multiples of C_2H_2 grouped together in the molecule of olefiant gas and hydrocarbons isomeric with it, or the multiples of C_5H_4 in the molecule of oil of turpentine and a large class of essential oils. *A complex organic molecule is thus represented as an association of two or more binary compounds, comparatively simple in constitution, often isolable substances and possessed of considerable stability.*

In the superior or chlorous portion of the formulæ of organic compounds we may generally expect to find chlorine, oxygen, nitrogen, hydrogen; and in the inferior or basic portion, carbon, or carbon and hydrogen. The former elements appear to be chlorous in the order in which they are enumerated :

Chlorine
Oxygen
Sulphur
Nitrogen
Hydrogen.

We find in substitutions, those in the lower part of the table replaced by those above them, hydrogen at the bottom of the table eminently so by chlorine at the top, and hydrogen also by oxygen. Nitrogen less frequently interferes, but it appears in certain cases more chlorous than oxygen and to replace that element; only, however, in certain double decompositions as an element of ammonia, which are not sufficient to determine its place, as oxygen might be placed above chlorine from similar indications, as the conversion of chloroform $FeCl_3$ into formic acid FeO_3 by potash.

Compounds of the same type.—These are bodies which have the same number of elementary atoms, and the same numbers of them chlorous and zincous. As :

Of olefiant gas type : olefiant gas $\frac{H_4}{C_4}$; chloride of carbon $\frac{Cl_4}{C_4}$.

Of ether type : ether $\frac{H_5O}{C_4}$; chloride of ethyl $\frac{H_5Cl}{C_4}$; chlorinated ethyl $\frac{H_4Cl_2}{C_4}$, &c.

Of alcohol type : alcohol $\frac{H_5O.O}{C_4.H}$; acetic acid $\frac{H_3O_3.O}{C_4.H}$; chloracetic acid $\frac{Cl_3O_3.O}{C_4.H}$.

Of aldehyde type : aldehyde $\frac{H_3O.O}{C_4.H}$; chloral $\frac{Cl_3O.O}{C_4.H}$.

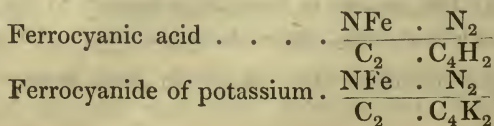
Ammonia.—The molecular formula of ammonia appears to be $\frac{N}{H_3}$, and not $\frac{H_3}{N}$. The hydrogen of ammonia being basic, according to the first formula, should not be replaced by chlorine, and certainly chlorinated salts of ammonia, analogous to the chlorinated compound ethers, have not been observed. Our knowledge of the composition of the explosive chloride of nitrogen is not sufficiently certain to decide the question. It will be remembered that N in the formula above is equivalent to O_3 or H_3 . Wöhler's white precipitate of mercury $HgCl + NH_3$ (page 656), and ordinary white precipitate, $HgCl + HgNH_2$, are assimilated, being expressed respectively by: $\frac{Cl.N}{Hg.H_3}$, and $\frac{Cl.N}{Hg.H_2Hg}$.

The black compound, produced by solution of ammonia upon calomel, is expressed by $\frac{Cl.N}{Hg_2.H_2Hg_2}$, or possibly by $\frac{ClHg.N}{Hg_2.H_2Hg}$. Thus amidogen is not necessarily present in the supposed metallic amides; but appears to be more necessary to the constitution of oxamide and urea, particularly the last. Of oxalate of ammonia, and oxamide, the molecular formulæ are: $\frac{O_3.O.N}{C_2.H.H_3}$ and $\frac{O_2N}{C_2.H_2}$.

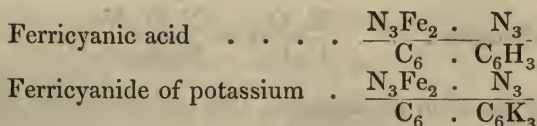
Cyanogen and cyanides.—The formula for cyanogen is

$\frac{N}{C_2}$; for hydrocyanic acid $\frac{NH}{C_2}$, and not $\frac{N}{C_2H}$. That the hydrogen of hydrocyanic acid is chlorous and not basic, appears in its being replaced by chlorine, with formation of hydrochloric acid and the chloride of cyanogen, $\frac{NCl}{C_2}$. Hence, also, the little action of potash and strong bases upon hydrocyanic acid (page 989), its hydrogen, unlike that of ordinary hydrogen acids, being chlorous, while the same hydrogen is readily replaced by the more chlorous metals, such as mercury, the cyanide of mercury being $\frac{NHg}{C_2}$. The latter salt is not decomposed by strong acids, as it would be if its constitution resembled that of cyanide of potassium $\frac{N}{C_2K}$. But cyanide of mercury is readily decomposed by sulphur and sulphuretted hydrogen, and by hydrochloric acid, sulphur and chlorine assuming the mercury and forming sulphuret and chloride of mercury respectively, while hydrogen is left in the place of the abstracted mercury, and hydrocyanic acid $\frac{NH}{C_2}$ reproduced.

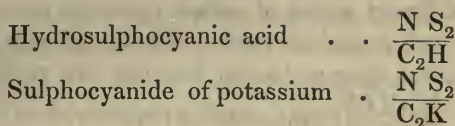
The two atoms of cyanide of hydrogen, which exist in *ferrocyanic acid*, $FeCy + 2HCy$, have, on the contrary, the constitution of an ordinary hydrogen-acid, the hydrogen being strongly basic and easily replaced by the basic metals, potassium &c. while the iron is not. It thus contains $\frac{N_2}{C_4H_2}$. But the iron of the associated cyanide of iron not being precipitated by potash (replaceable by potassium), must be chlorous; and this metallic cyanide, therefore, resembles ordinary hydrocyanic acid in constitution, or is $\frac{NFe}{C_2}$.



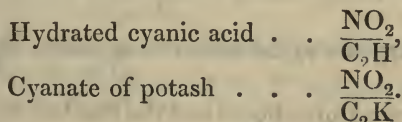
The molecular formulæ for *ferricyanic acid* ($H_3 + Fe_2Cy_6$), and for *ferricyanide of potassium* ($K_3 + Fe_2Cy_6$), deducible from the same principles, are :



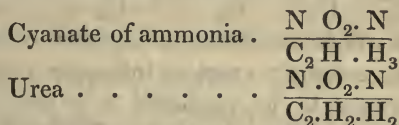
Assigning to *sulphocyanogen*, C_2NS_2 , the molecular formula $\frac{\text{NS}_2}{\text{C}_2}$, its compounds will be :



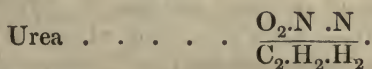
Hydrated *cyanic acid* and cyanate of potash will be represented by formulæ which assimilate them to the preceding compounds:



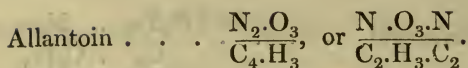
The two isomeric bodies *cyanate of ammonia* and *urea* (page 392) have different molecular formulæ :



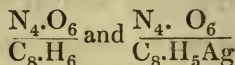
In the last formula urea is represented as containing 1 atom of cyanogen, 2 atoms of water and 1 atom of amidogen. According to the more common opinion, it contains 2 atoms of carbonic oxide and 2 atoms of amidogen, a view which may be expressed by making a slight change in the upper line of the preceding formula :



But the existence of cyanogen in urea being probable, the first formula is preferable. Urea may then be compared with *allantoin*, which contains 2 atoms of cyanogen and 3 atoms of water :



Doubling the atom of allantoin, that substance and its compound with oxide of silver will be :



From the different action of potash upon the isomeric bodies, *Dutch liquid* and *protochlorinated chloride of ethyl*, there can be little doubt but their molecular formulæ are really different :

Dutch liquid $\frac{\text{H}_3 \text{Cl} \cdot \text{Cl}}{\text{C}_4 \cdot \text{H}}$; *protochlorinated chloride of ethyl* $\frac{\text{H}_4 \text{Cl}_2}{\text{C}_4}$;

and while the other chlorinated compounds of chloride of ethyl are $\frac{\text{H}_3 \text{Cl}_3}{\text{C}_4}$ and $\frac{\text{H}_2 \text{Cl}_4}{\text{C}_4}$, those of olefiant gas, isomeric with the pre-

ceding, are, as appears by the action of an alkali, $\frac{\text{H}_2 \text{Cl}_2 \cdot \text{Cl}}{\text{C}_4 \cdot \text{H}}$, and

$\frac{\text{HCl}_3 \cdot \text{Cl}}{\text{C}_4 \cdot \text{H}}$. For from *Dutch liquid* and the two last mentioned com-

pounds, potash withdraws HCl , and liberates three compounds of the same type : $\frac{\text{H}_3 \text{Cl}}{\text{C}_4}$, $\frac{\text{H}_2 \text{Cl}_2}{\text{C}_4}$ and $\frac{\text{HCl}_3}{\text{C}_4}$.

The elements which are chlorous together or basic together in a compound, certainly exert an influence upon each other, although they are not to be supposed to be combined, as those of different name are with each other. For we find a tendency among them to arrange themselves in pairs. Thus the chlorinated compound of oxide of ethyl, most readily formed, is that of which the empirical formula is $\text{C}_4 \text{H}_3 \text{Cl}_2 \text{O}$, and the molecular formula $\frac{\text{H}_3 \text{Cl}_2 \text{O}}{\text{C}_4}$, or rather $\frac{\text{H}_2 \text{Cl}_2 \text{HO}}{\text{C}_4}$, of which the three atoms of hydrogen are associated with three still more chlorous atoms namely two of chlorine and one of oxygen. There can be no doubt that these three remaining atoms of hydrogen are thus in some degree defended from the farther action of chlorine, and less easily removed than the other two.

The molecular formula of oil of bitter almonds, or hydruret of benzoyl appears to be $\frac{\text{H}_6 \text{O}_2}{\text{C}_{14}}$; of hydrated benzoic acid $\frac{\text{H}_5 \text{O}_3 \cdot \text{O}}{\text{C}_{14} \cdot \text{H}}$.

Of the *oil of spiræa* or *salicylous acid*, which is isomeric with the last, $\frac{H_5O_4}{C_{14}H}$; of *chlorosalicylous acid*, $\frac{H_4O_4Cl}{C_{14}H}$; and of hydrated *salicylic acid*, $\frac{H_5O_6}{C_{14}H}$, or $\frac{H_5O_5 \cdot O}{C_{14} \cdot H}$.

The peculiarity of oil of spiræa, or salicylous acid, is that its single basic atom of hydrogen is removeable by itself, like that of a hydrogen acid, in the formation of salts, while of hydrated benzoic acid, both H and O are removed in the formation of salts. This difference is expressed in their molecular formulæ.

The hydrated and bibasic *bromobenzoic acid* is an association of two acids, one of which differs from the other in having an atom of hydrogen replaced by bromine; namely $HO + C_{14}H_5O_4$ and $HO + C_{14}H_4BrO_4$. Of these two the molecular formulæ may be, of the first, $\frac{H_5O_4 \cdot O}{C_{14} \cdot H}$ and of the second $\frac{H_4O_4Br \cdot O}{C_{14} \cdot H}$.

Of *benzamide*, $Bz + Ad$, or $C_{14}H_5O_2 + NH_2$, the molecular formula may be $\frac{H_5N \cdot O_2}{C_{14}H_2}$, in which N replaces 3O of hydrated benzoic acid.

Of *hydrobenzamide*, $C_{14}H_6N_3$, produced by the action of ammonia on the hydruret of benzoyl, the molecular formula is $\frac{H_6N_3}{C_{14}}$; or that of the oil, with 2O replaced by N_3 .

Of *salicylimide*, $HO + C_{14}H_5ON_3$, produced by the action of ammonia on salicylous acid, $\frac{H_5O_2N_3}{C_{14}H}$, or $\frac{H_5N_3 \cdot O \cdot O}{C_{14} \cdot H}$; that is, salicylous acid with 2O replaced by N_3 .

Of *chlorosalicylimide*, $C_{14}H_3Cl_3O_2N_3$, $\frac{H_2Cl_3N_3O_2}{C_{14}H}$, or $\frac{Cl_3H_2O_2N_3}{C_{14}H}$; three atoms of the chlorous hydrogen of salicylimide being replaced by chlorine.

Formation of acids.—The formula of benzole or benzin, is $\frac{H}{C_{12}}$; of the neutral body, sulphobenzide, $\frac{H_5SO_2}{C_{12}}$, or $\frac{H_5O_2}{C_{12}S}$. To the last hydrated sulphuric acid is attached, in *sulphobenzic acid* $= \frac{H_5O_2 \cdot O_3 \cdot O}{C_{12}S \cdot S \cdot H}$, or $\frac{H_5SO_2 \cdot O_3 \cdot O}{C_{12} \cdot S \cdot H}$.

Sulphurous acid, SO_2 , is a body like sulphobenzide; in hy-

posulphuric acid it has hydrate of sulphuric acid attached to it. Sulphurous acid, $\frac{O_2}{S}$; hydrated hyposulphuric acid, $\frac{O_2 \cdot O_3 \cdot O}{S \cdot S \cdot H}$

The neutral substance, *benzile*, $C_{14}H_5O_2$, or $C_{28}H_{10}O_4$, becomes benzilate of potash, by fixing the elements of hydrate of potash; thus benzile, $\frac{H_{10}O_4}{C_{28}}$; benzilate of potash, $\frac{H_{10}O_4 \cdot O \cdot O}{C_{28} \cdot H \cdot K}$

When the potash is withdrawn from the latter by a stronger acid, hydrated benzilic acid is formed, $\frac{H_{10}O_4 \cdot O \cdot O}{C_{28} \cdot H \cdot H}$. When neutralised with bases, this hydrate loses an atom of water and acquires an atom of metallic oxide in its place.

Chlorisatin, a neutral substance, when dissolved in caustic potash is converted into chlorisatinate of potash, in a similar manner: Chlorisatin, $\frac{H_4ClO_3N}{C_{32}}$; chlorisatinate of potash,

$\frac{H_4ClO_3N \cdot O \cdot O}{C_{16} \cdot H \cdot K}$. Decomposed by a strong acid, the latter salt gives hydrate of *chlorisatinic acid*, $\frac{H_4ClO_3N \cdot O \cdot O}{C_{16} \cdot H \cdot H}$

Concentrated acids decompose this hydrate, assuming its water, and reproduce the neutral chlorisatin. It is clear that the anhydrous acids generally, such as SO_3 , PO_5 , &c., belong to the class of sulphobenzide and chlorisatin, and owe their power of combining with bases to the association with them of an atom of water.

Hydrate of sulphuric acid, $\frac{O_3 \cdot O}{S \cdot H}$; hydrates of phosphoric acid, $\frac{O_4 \cdot O}{P \cdot H}$, $\frac{O_5 \cdot O_2}{P \cdot H_2}$ and $\frac{O_5 \cdot O_3}{P \cdot H_3}$.

We have other series of compounds of which the members only differ from each other, in containing different proportions of water or its elements attached to a common basis, as starch, gum and starch sugar; gum being starch plus 1 atom of water; and starch sugar, starch plus 2 atoms of water. It is at present impossible, however, to assign a probable molecular formula to the basis of the starch and many other series of compounds, from our ignorance of the function of the hydrogen in their constitution, where the hydrogen has not been replaced by another element more decidedly chlorous or basic in its character.

CHAPTER II.

SECTION I.

AMYLACEOUS AND SACCHARINE SUBSTANCES.

STARCH.

Syn. FECULA, AMYLIN; $C_{12}H_{10}O_{10}$; in combination with oxide of lead, $C_{12}H_9O_9 + 2PbO$, (Payen). Its composition, well dried in vacuo at 212° , is

12 atoms of carbon. . . .	917.22..	44.91
10 atoms of hydrogen. . . .	125.00..	6.11
10 atoms of oxygen. . . .	1000.00..	48.98
	<hr/>	
	204.22..	100.00

Starch is separated from a variety of vegetable substances containing it, from the grains of the different cereals, many roots such as the potato, the stems of many monocotyledonous plants particularly the palms, and from several lichens. It is contained in the cavities of the vegetable cells, in the form of small white and brilliant grains, which are not crystalline, but have a rounded outline without any determinate form. It is so far an organised substance, that each grain has a species of envelope, which resists the action of cold water, while the inner portion is observed by the microscope to be composed of concentric layers of unequal thickness, as if the layers produced during the day exceeded in thickness those formed during the night. (Fritzsche). The grains of the starch of different plants differ in size, those of the potato being about $\frac{7}{100}$, of wheat $\frac{8}{100}$, of millet, $\frac{1}{100}$ th of an inch in diameter, according to observations of Raspail. But it is also known that the starch grains of the same plant differ in size at different stages of its development.

The purest starch is obtained from potatoes, which are reduced to a pulp and washed on a sieve. The grains of starch are separated and passed through; they may be washed repeatedly with cold water. Potatoes yield 15 to 17 per cent. of starch; wheaten flour consists essentially of starch and another vegetable principle gluten. When made into dough with a little cold water, inclosed in a linen bag, and gently pressed by the hand in water, so long as a milky juice exudes, these two subs-

tances are in a great measure separated, the gluten remaining in the bag, and the grains of starch being diffused through the water, from which they afterwards subside. On the large scale, wheaten meal coarsely ground is mixed with cold water in large vats, in which, with a certain addition of sour water from a former process, the liquid ferments for seven or eight days, and the starch subsides. The acetic acid formed in the fermentation dissolves the greater part of the gluten of the flour, and the bran is separated from the starch by a fine sieve. The starch is afterwards mixed with pure water in the vat and allowed to settle; the remaining gluten is deposited as a grey slimy matter above the starch, which is removed, and the starch washed again till pure. For the fermentation, the action of a weak solution of caustic alkali has lately been substituted, by which the gluten of flour is dissolved and the starch left. Mr. O. Jones employs a ley containing 200 grains of caustic soda in one gallon of water. A ley containing 400 grains of soda causes the starch to gelatinize; by that quantity of ley, one pound of excellent starch is obtained from flour of rice, allowed to digest in it in the cold for forty-eight hours.

Arrow root is the starch from the root of the *marantha arundinacea*. It is not accompanied by any odoriferous principle, and has therefore no smell when boiled with water, in which respect it resembles potato starch washed with alcohol. *Sago* is derived from the pith of true palms of the genus *Sagus*; *tapioca* or *cassava*, from an American plant, the *iatropha manihot*, of which the milky juice, itself poisonous, deposits when diffused through water a harmless starch. The peculiar appearance and solubility in cold water of sago and tapioca arise from the starch being exposed while humid to a temperature above 140° , so that it is dried in the gelatinous condition and not in the original grains.

Starch or fecula may be purified from adhering gluten by maceration in diluted acetic acid, or by means of a cold and dilute solution of alkali. The starch of commerce is perfectly white, and in small columns formed by the contraction of the humid mass of starch in drying, which are easily reduced to a fine powder. It emits a particular sound when pressed between the fingers, its density is 1.53. The other characters which fecula exhibits are complete insolubility in cold water and in

alcohol, but resolving itself in boiling water into a mucilaginous liquid, which forms a jelly on cooling. This when suddenly dried upon linen imparts considerable stiffness to it. Dilute acids dissolve starch, and form a transparent and highly fluid liquid. When this solution is boiled for a long time, the starch is first converted into a body having the properties of gum, and afterwards into starch sugar. Nitric acid with the assistance of heat converts starch into oxalic and malic acids, without producing a trace of mucic acid. Starch is also soluble in alkalies; when brayed with a concentrated solution of hydrate of potash, it forms a transparent gelatinous compound soluble in alcohol and water, from which the starch is precipitated by acids. Starch is precipitated from solution by lime water and hydrate of barytes, and by sub-acetate of lead containing ammonia, forming insoluble compounds with lime, barytes and oxide of lead. A solution of starch is also coagulated by borax, which combines with and precipitates the starch, but not by boracic acid. Starch is precipitated by an infusion of gallnuts. It forms a blue insoluble compound with iodine.

Gelatinous starch or amidin.—In this state starch appears to retain a portion of its organisation or structure, upon which some of its properties depend, and which is the cause of the difference in properties of the varieties of starch, containing the same chemical principle. When grains of fecula are rubbed in a mortar with sand, their coating is broken and they form a greyish white powder, which when mixed with a little cold water immediately expands and forms a transparent jelly. If the uninjured grains be thrown into water above 140° , they imbibe water, swell and burst their envelopes, which have a certain degree of elasticity, and undergo the same change. But the gelatinous starch has imbibed water like a sponge, without being dissolved and when placed upon several folds of blotting paper imparts to the latter its moisture, and dries up into a mass resembling horn, which exhibits again the same phenomena, when after being reduced to powder it is treated with boiling water. A portion of the gelatinous starch, however, appears to be dissolved by a large quantity of cold water, about $\frac{1}{4}$ th of the starch, when the bruised grains are diffused through 100 times their weight of cold water, and the whole of it when gelatinous starch is boiled with 40 or 50 parts of water; for the mucilaginous liquid passes through a double paper filter and no

granules or solid matter in any other form can be perceived in the liquid by the microscope. The tegumentary portion of the starch, which amounts to three or four thousands of the whole, remains on the filter, but may also be dissolved by continued boiling. When the quantity of starch dissolved by hot water is considerable, much of the starch separates in a gelatinous state, on the cooling of the solution. The peculiar character of the solution of starch in water has been the object of much research by M. Payen, which lead to the observation that by the freezing of a solution of starch that substance separates from the water and contracts into a species of tissue, which is not dissolved again on the thawing of the ice. It is the opinion of the same chemist that the organisation of the starch is not altogether effaced or its cohesion destroyed, so long as it is gelatinous and possesses the property of being stained by iodine of a blue, or of different shades of violet to red, according to the degree of its division.*

Granules of starch of M. Jacquelin.—When starch is heated under pressure in a Papin's digester to 302° (150° cent.), with from five to fifteen times its weight of water for two hours, the whole is dissolved except the tegumentary matter, and the solution is so thin that it may be filtered at the boiling temperature. This solution when it cools deposits a considerable mass of pulverulent matter, white and opaque and entirely composed of a species of granules, first observed by M. Jacquelin. These granules when examined by a microscope having a power of 200 diameters, present themselves as circular or spherical bodies, transparent, and uniformly $\frac{1}{100}$ of an inch ($\frac{1}{1000}$ ths of a millimetre) in diameter. When dried they have the whiteness of starch without its lustre. They are denser than water, and subside from that liquid almost as quickly as fecula. These granules are scarcely soluble at 32° , slightly so at 53.6° , but dissolve in a considerable proportion about 158° , and in still greater quantity at the temperature of ebullition. This increased solubility is the most remarkable chemical change which the starch has undergone, by its solution in water at a high temperature. Anhydrous alcohol precipitates completely a solution of the granules and the aqueous solution of iodine

* Annales de Chimie et de Physique, tome 65, p. 225.

makes it blue and not purple. When a film of a concentrated solution of these granules is left under the microscope, it is seen to be in a state of agitation so long as the evaporation of the water continues and when the matter comes to be dried, the granules cease to be visible, attaching themselves to each other as if soldered together, and forming a transparent plate in which nothing can be perceived even with a magnifying power of 800 diameters. A solution of the granules, when frozen and afterwards melted, gives the granules in the form of fine filaments, which are very short, and have a silky lustre. M. Jacquelin finds these granules and fecula, both dried between 266° and 275° , to have the same composition, $C_{12}H_{10}O_{10}$. But he constantly obtained a small quantity of nitrogen from starch, about $\frac{1}{4}$ per cent. from his granules and a somewhat larger proportion from fecula, which he conceives to be essential to that substance. The power which starch possesses to form these granules, must be considered as an organic property, and proves that it retains contractility, even when dissolved in water.* The original grains of fecula, which consist of concentric layers, are still more highly organised; starch indeed occupies an important place in organic chemistry, as a link between matters truly organised and those bodies of a less complex constitution, which still belong to the organic kingdom, but approach in their crystallization, volatility or chemical properties to mineral substances properly so called.

A compound of amidin and oxide of lead was formed by M. Payen, by dissolving two parts of pure starch in 250 parts of water, with ebullition for twenty minutes and pouring the filtered solution into an excess of the ammoniacal solution of acetate of lead (page 594), collecting and washing the precipitate upon a filter, and drying it in vacuo at 356° (180° cent.) He terms it the bibasic amyrate of lead, $C_{12}H_9O_9 + 2PbO$.

Starch combines with chlorine, bromine and iodine. The solution of chlorine has little effect upon starch, but when dry, starch is introduced into chlorine gas, the latter is absorbed, a little carbonic acid is evolved, the mass becomes liquid, assumes a brown colour, and is charged with much hydrochloric acid. The *bromide of starch* is an orange powder, which is formed, ac-

* Jacquelin, Annales de Chimie et de Physique, tome 73, p. 167.

cording to Fritzsche, when water saturated with bromine is dropt into a solution of starch in water acidulated with hydrochloric acid. The colour is destroyed by a slight heat; to obtain the *iodide of starch* in a state of purity the following process is recommended. A firm jelly is prepared by boiling potato starch with water, and after cooling, a quantity of hydrochloric acid is added sufficient to occasion the mixture to become liquid when assisted by a slight elevation of temperature. The solution is then filtered and a solution of iodine in alcohol is mixed with it, so long as the latter produces a blue precipitate, care being taken not to add too much of the solution of iodine, as the alcohol of that solution will then precipitate uncombined starch. The precipitate is collected, drained on a filter and washed with water poured upon it in small quantities. Once deprived of hydrochloric acid, the compound dissolves in the water used to wash it; the washing is therefore interrupted so soon as the liquid which passes exhibits an intense blue colour; the compound is removed from the filter and dried on a capsule over sulphuric acid in vacuo. A brown-black gummy and very brilliant mass is thus obtained, which can easily be pounded when perfectly dry, but which becomes viscous by attracting hygrometric moisture. It is very easily dissolved by water, giving a deep blue solution, and may be recovered again by evaporation in vacuo, in a dry state and without alteration. When a solution of iodide of starch is heated, it becomes colourless at 158° or 160° if very dilute, but not under 194° when the solution is concentrated. The colour reappears on the cooling of the solution, provided it has not been boiled. When the colour is not restored, the iodine appears to be converted into iodic and hydriodic acids. Animal charcoal discolours the blue solution, carrying down iodine. The iodide of starch contains 41.79 parts of iodine with 58.21 of starch, according to the analysis of Lassaigne, or it consists of two atoms of iodine with one atom of starch. (Berzelius).

Dextrin or mucilaginous starch.—By the action of acids, alkalies, diastase, and of heat, a complete dissolution of the gelatinous starch may be effected; it becomes largely soluble in cold water, the solution is mucilaginous and not gelatinous, and the altered starch has many of the characters of gum. Dextrin

is prepared by boiling a solution of starch with a few drops of sulphuric acid, or by heating to 200° , 100 parts of starch, 20 of sulphuric acid and 28 of water, filtering and precipitating by alcohol, as a white glutinous substance becoming pulverulent by repeated washings with alcohol. It may also be prepared by diastase; an infusion of malt is mixed with a solution of starch, in the proportion of 6 or 8 of malt to 100 starch, and the liquid kept at 150° for twenty minutes. From being milky and viscid, it becomes nearly as fluid as water. It is then heated quickly to 212° , to stop the farther action of the diastase, filtered and precipitated by alcohol. The solution of dextrin was supposed not to be affected by iodine, but Jacquelin finds that dextrin is coloured purple by iodine, and not blue, like fecula, or that is not colourable by iodine, according to the circumstances of its preparation. Thus 1 part of the granules with 5 parts of water, heated to 320° for forty-five minutes, gave a dextrin which was colourable purple by iodine; while the same materials heated for one hour and forty-five minutes, at the same temperature, gave a dextrin not colourable by iodine. There can be little doubt, therefore, that there are two varieties of dextrin, *dextrin colourable by iodine*, and *dextrin not colourable by iodine*. These varieties of dextrin also appear in the succession of changes which fecula undergoes under the influence of an acid. Thus a mixture of 1 part of fecula with 1 part of water and $\frac{1}{10}$ of oxalic acid, gave when heated at 266° for twenty minutes, dextrin colourable purple, for one hour dextrin not colourable, for two hours sugar of starch also not colourable.

Dextrin is not fermentable by yeast, but is readily convertible by diastase and dilute acids into a sugar, which is fermentable. The name dextrin was applied to it by Biot from its effect upon a ray of polarised light passing through its solution, in causing the plane of polarisation to deviate very considerably to the right.* The composition of dextrin according to M. Payen,

* Memoirs by M. Biot, on Circular Polarisation; Taylor's Scientific Memoirs, vol. 1 pp. 584, 600, and Annales de Chimie et de Physique, tomes 69, p. 22, et 74, p. 401. When light polarised by reflection from the surface of a plate of black glass or from the surface of a pile of superposed plates of transparent glass reaches the eye through a disc of tourmalin, a solution of dextrin being interposed in a tube between the reflecting plate and tourmalin, the light does not disappear in those positions of the tourmalin in which light would be completely absorbed without the interposition of the solution of dextrin; but prismatic colours are

is $C_{12}H_{10}O_{10}$, and of two dextrinates of lead dried at 356° , $C_{12}H_9O_9 + PbO$, and $C_{12}H_9O_9 + 2PbO$, so that dextrin is identical in composition with amidin, both when free and in combination. Both of the dextrinates of lead retain 1 eq. of water, when dried at inferior temperatures. A dextrinate of barytes, prepared by Payen by means of a solution of anhydrous barytes in wood spirit, and strongly dried between 356° and 374° , gave $C_{12}H_9O_9 + BaO, HO$.

When dry starch is heated in an oven it becomes brown and soluble in cold water. It then forms *British gum*, which corresponds in properties with dextrin.

Diastase.—This is a remarkable substance observed by Payen and Persoz in grains and seeds, but only after germination, and in the tubers of the potato near the places from which the shoots proceed. The production of diastase is the principal object of the malting of grain or permitting it to germinate, and has an important influence upon the changes which occur in the starch of grain in brewing. Diastase is prepared by moistening freshly germinated barley with half its weight of cold water, and submitting it to pressure, by which a viscid liquid is obtained. This liquid is filtered and then heated to 158° , which causes the greater part of an azotised or albuminous matter existing in the liquid to be coagulated and separated. The liquid after filtration is mixed with a sufficient quantity of alcohol to precipitate the diastase and retain in solution the colouring matter, sugar and foreign azotised matter present. The precipitated diastase is washed with alcohol, dissolved again in water and thrown down by alcohol two several times, for the purpose of purifying it (*An. de Chi. &c.*, liii, 73). When dried it is a white solid amorphous substance, soluble in water, but insipid, and not precipitated by subacetate of lead. It contains nitrogen, and has some analogy to gluten, but has not been obtained in a state of sufficient purity for

produced which follow a certain order, if the plane of polarisation is turned from left to right. It is by the order of these colours, that a liquid is said to polarise light to the right or to the left. The solution of starch polarises to the right and that of dextrin considerably more so in the same direction. While a solution of cane sugar produces the succession of colours in an inverse order, and is said therefore to polarise to the left. The progress of chemical changes may thus often be observed in a solution of starch, the juices of plants and other organic fluids.

analysis. Malted barley contains not more than 1—500th of its weight of diastase. The solution of diastase has no action upon many vegetable principles, such as sugar, gum, albumen and gluten, but has a specific action upon starch, converting a solution of that substance first into dextrin, and afterwards into the sugar of starch, and such is its energy that 1 part of diastase will convert 2000 parts of starch into sugar. Diastase acts upon gelatinous starch even at 32° , but most powerfully between 140° and 150° . It has the remarkable property of separating the envelope from the grains of starch.*

In the ordinary process of brewing, the mashing or infusing of the malt should be begun at 168° or 170° , the temperature at which the diastase acts more advantageously, by which the starch of the grain is converted into sweet worts. The temperature may be afterwards raised by adding water at 185° or 195° to the mash tun; the saccharisation is generally completed in an hour and a half at the utmost, and the sweet worts are then run into a copper to be boiled and hopped, (Black on Brewing). The sugar of the cooled worts is afterwards fermented by the action of another principle yeast and converted into carbonic acid and alcohol, as will afterwards appear. The diastase of 1 part of malt is often made to saccharise the starch of 10 or 12 parts of unmalted grain, when the sweet wort is to be fermented and distilled for spirits.

Gluten.—This substance remains when the starch of wheat flour has been separated by pressing the dough in water till the washings are no longer milky, as a grey viscid adhesive and elastic substance. It is insoluble in water, but is dissolved by alkalies and also by acetic acid. It contains nitrogen, and when left humid in air, has a tendency to putrify; when completely dry it is hard and brittle, with some resemblance to glue. Gluten forms from 19 to 24 per cent of good wheaten flour. According to Davy the wheat grown in the south of Europe is richer in gluten than that of colder climates; it is peculiarly suitable on that account for the manufacture of macaroni, vermicelli and similar pastes, which are made by a kind of wire drawing. Gluten is one of the most nutritive of vegetable substances; when se-

* The name diastase was applied to it from *διαστημι*, I separate, in reference to its property of separating two supposed constituents of starch.

pared however from starch and pure, gluten is scarcely digestible.

It is to the presence of gluten that wheat flour owes its property of forming a tenacious paste with water, and also a light spongy bread. In baking leavened or loaf bread, the dough is mixed with a quantity of yeast, or in its absence with a portion of sour dough called leaven, and set aside in a warm place, which occasions the saccharine matter of the flour to undergo the vinous fermentation. The carbonic acid gas then evolved expands the gluten into vesicles and causes the *rising* the dough, which then forms a light loaf when heated in the oven.

Gluten is not a pure principle; when digested in hot alcohol till every thing soluble is taken up, it leaves a bulky substance of a greyish colour which has been called *vegetable albumen*. The latter is soluble in water, but when the solution is heated the albumen coagulates and becomes insoluble; it is also coagulated by the stronger acids. The true gluten, obtained by evaporating the alcoholic solution, retains its adhesive property and is soluble both in acids and alkalies. It is not precipitated from a solution in acetic acid by the acetate of lead or persulphate of iron, but abundantly by the chloride of mercury and infusion of gallnuts.

Inulin.—This variety of starch was discovered by V. Rose in the root of the *Inula Helenium*, to which it owes its name. It is also found in various other roots, and in some lichens. It is conveniently obtained from the roots of the dahlia. The latter are rasped, washed with cold water and expressed, then boiled with water, and the hot solution filtered through linen. This solution may be clarified by white of egg, if muddy, evaporated till a pellicle forms on its surface, and then allowed to cool; the inulin is deposited in a pulverulent form. It is collected on a filter and washed well with cold water. Inulin is a very fine white tasteless powder, of density 1.336, very soluble in boiling water, but not gelatinizing, and requiring 50 parts of cold water to dissolve it. Iodine makes it yellow, and insoluble in cold water. It is insoluble in cold alcohol, soluble in acids, which change it with the aid of ebullition into sugar, and more readily than ordinary starch. It is converted by nitric acid into malic and oxalic acids, without a trace of mucic acid. It was found

by Mr. E. A. Parnell, when dried at 212° , to consist of $C_{24} H_{21} O_{21}$. Two compounds which it forms with oxide of lead are thus constituted, $C_{24} H_{21} O_{21} + 5PbO$, and $C_{24} H_{18} O_{18} + 3PbO$.*

Lichen starch.—Several species of lichens, particularly the *Cetraria Islandica* (Iceland moss), contain a variety of starch, closely resembling common starch. It gives a white and opaque jelly. It is feebly coloured by iodine, the tint produced being between brown and green. This starch contains, according to the analysis of Guerin-Vary, $C_{10} H_{11} O_{10}$, but this result requires confirmation,

SUGARS.

Several substances are known as sugars which agree in having a sweet taste, but differ in other respects. Those which undergo a peculiar decomposition and are converted into carbonic acid and alcohol, when their solution is mixed with yeast, are fermentable sugars, and form the most important class; they are Cane sugar, Grape and Starch sugar, which appear to be identical, Milk sugar, Mushroom sugar, and the insipid sugar of Thenard, of which the two first-mentioned varieties are the most abundant and best understood.

CANE SUGAR, OR ORDINARY SUGAR,

Its formula in the crystallised state is $C_{12} H_{11} O_{11}$; in combination with oxide of lead, $C_{12} H_9 O_9 + 2PbO$ (Peligot).

Loaf sugar, sugar-candy, or the purest granular muscovado may be taken to represent this species. It exists in many plants, but is derived in large quantity only from the juice of the sugar-cane, from beet-root and the maple-tree. These juices are rapidly evaporated with a small addition of lime, to neutralise free acid, being sometimes clarified first by albumen, and afford on cooling a brown granular sugar, from which a dark coloured syrup, molasses, separates. The latter contains a portion of crystallizable sugar, which may be separated from it by evaporation, and leaves treacle, which differs in taste from crystallizable sugar, and is certainly a distinct species of sugar, although highly impure. To refine sugar, it is dissolved in

* Phil. Mag. 3rd series, vol. 17, p. 126.

water, and the solution generally filtered hot through a bed of animal charcoal in grains like gunpowder, and about two feet in thickness. The colourless syrup thus obtained is evaporated in vacuo, about 150° , in close pans heated by steam, from which the vapour is constantly withdrawn by an air-pump. When sufficiently concentrated, the syrup is run into a cooler, and agitated by an oar to promote its granulation.

It is then transferred into moulds, which are inverted cones, having an aperture in the apex, and kept in a warm place, while the dark coloured and uncrystallizable syrup drains off; a strong syrup of pure sugar being poured on the upper surface to percolate downwards and remove the last portions of the former. Instead of the pure syrup, moist pipé-clay was formerly placed on the surface of the sugar for the same purpose, and is still employed in clayed sugars. The loaf sugar from these moulds is a white compact mass, composed of small crystals. A strong solution of it, evaporated slowly, affords large transparent and colourless crystals of sugar-candy, of which the form is an oblique prism of a square base, or a six-sided prism with dihedral summits. The density of pure sugar is 1.5629 (Thomson).

Loaf sugar diffuses a phosphorescent light when broken in the dark. It is unalterable in dry air, and loses nothing but a trace of hygroscopic water when heated. It fuses at 356° (180° cent.) and forms a thick tenacious liquid, which becomes a transparent vitreous mass on cooling (barley-sugar). The latter changes after a time, and rapidly when damp, into an opaque mass, which exhibits when broken, the crystalline facets of ordinary sugar. Sugar is soluble in one third of its weight of cold, and in all proportions of boiling water. Its power to crystallise is destroyed by keeping its solution for some time boiling, and also by the addition of $\frac{1}{10}$ th of its weight of oxalic, citric, or malic acid, which instantly render a viscid and boiling syrup, very fluid. Sugar dissolves in 80 parts of absolute alcohol at the boiling temperature, very slightly in the same cold, in 4 parts of alcohol of density 0.830, and is wholly insoluble in ether, which precipitates sugar from its solutions. Sugar is nutritive when accompanied with other aliments, but is incapable alone of supporting life for any length of time, in common with all organic principles destitute of nitrogen. A solution of sugar placed in contact with the stomach of the calf (rennet),

is changed entirely into lactic acid, according to the observations of Fremy.

A solution of cane sugar is fermented by yeast, but not so readily as grape sugar; indeed the first action of the yeast is to convert cane sugar into grape sugar, which appears to be the only species of sugar that is directly fermentable (H. Rose); diluted sulphuric acid with heat, and tartaric acid likewise effect the latter transformation of cane sugar. The first action of caustic potash in excess upon cane sugar, at the boiling temperature, is similar. A strong syrup mixed with undiluted oil of vitriol becomes hot, swells up, much charcoal is formed, and sulphurous and formic acids disengaged. Sugar is also decomposed by hydrochloric acid, with the aid of heat, and charcoal liberated. Nitric acid converts it into saccharic, oxalic and carbonic acids, 100 parts of sugar yielding 67 parts of oxalic acid, according to Thenard. Dry chlorine has no action on dry sugar, but syrup absorbs chlorine slowly, and the sugar is converted, with disengagement of carbonic acid, into a brown matter, which retains some hydrochloric acid. Sugar dissolves carbonate of copper and verdigris, forming green solutions, which are not precipitated by alkalies; the salts, both of copper and peroxide of iron, cease to be precipitated by alkalies when sugar is added to them. Sugar also dissolves lime, barytes and oxide of lead in large quantities, and forms definite compounds with these bases, although in no respect an acid. Sugar is generally viewed as containing two atoms of water of crystallization, which cannot be expelled by heat, without destroying the sugar, but one or both of which are separated in these compounds and replaced by a metallic oxide.

Compound of sugar and lime; $C_{12} H_9 O_9 + CaO, HO$ (Peligot). When a solution of sugar is digested by a moderate heat with hydrate of lime, a bitter alkaline solution is obtained, in which 100 parts of sugar are united with 56 of lime. The compound is less soluble at a high temperature, and the solution, when boiled, becomes a thick gelatinous mass, from which the compound separates as a precipitate, and may be obtained pure by washing with boiling water, in which it is insoluble, or by precipitation with alcohol, which retains any excess of sugar. The solution of this compound absorbs carbonic acid rapidly from the air, and acute rhombohedral crystals of hydrated car-

bonate of lime form in it. The compound of *sugar and barytes* is similar, according to Peligot's analysis, as corrected by Liebig, or $C_{12} H_9 O_9 + BaO, HO$. The compound of *sugar and oxide of lead*, $C_{12} H_9 O_9 + PbO$, is prepared by dissolving oxide of lead in a boiling solution of sugar; it falls as a white precipitate, which is had perfectly pure by washing it with boiling water, which does not dissolve it, and drying; a soluble compound of sugar and oxide of lead is retained in the liquor which gives the precipitate. A crystalline compound of *sugar and chloride of sodium* is formed on allowing a solution of 1 part of common salt and 4 parts of sugar to evaporate spontaneously in air, the solution being decanted several times from the crystals of sugar-candy, which are first deposited. The crystals of the compound in question have a taste at once sweet and saline, and run into a liquid in humid air; their formula is $2 C_{12} H_9 O_9 + Na Cl, 3HO$.* It is probable from the composition of this salt, that the usual equivalent of sugar should be multiplied by two, if not by a higher number.

Caramel, $C_{12} H_9 O_9$. At a temperature a little above its point of fusion $356^\circ (180^\circ \text{ cent.})$, sugar becomes brown, and at 410° or $428^\circ (210^\circ \text{ or } 220^\circ \text{ cent.})$ swells up and becomes a black porous shining mass, which is known as caramel, losing nothing but two atoms of water. It is obtained free from sugar, and the bitter products which accompany the caramel of the shops, by solution of the black mass in a small quantity of water, and precipitation of the caramel by alcohol, which retains the impurities in solution. Caramel is a black or very dark brown powder, neutral and insipid, soluble in water, to which it gives a fine colour of sepia, and not fermentable. It has the same composition as sugar in the compound of sugar and lead, $C_{12} H_9 O_9$ (Peligot); it precipitates salts of barytes and basic salts of lead. Grape sugar furnishes the same product by heat. At a higher temperature, caramel loses more water, and forms an insoluble matter; when still more strongly heated it affords combustible gases, and leaves a bulky charcoal, difficult of incineration.

Metacetone, $C_6 H_5 O$ (Fremy), a combustible liquid, obtained mixed with acetone, by distilling a mixture of 1 part of sugar

* Peligot; Recherches sur la nature et les propriétés chimiques des sucres, An. de Ch. &c. t. 67, p. 113; et sur la composition du saccharate de plomb. *Ib.* t. 73, p. 103.

with 8 parts of well pulverised quick-lime. The metacetone is insoluble in water, by means of which it may be freed from acetone. It is a colourless liquid, of an agreeable odour, boiling about 183.2° (84° cent.), and miscible with alcohol and ether. It may be viewed as acetone, minus one atom of water, $C_6 H_6 O_2 - HO = C_6 H_5 O$. One atom of anhydrous sugar contains the elements of:

1 atom of acetone.	.	.	C_3	H_3	O
1 atom of metacetone	.	.	C_6	H_5	O
3 atoms of carbonic acid.	.	.	C_2		O_6
1 atom of water.	.	.		H	O
<hr/>					
			C_{12}	H_9	O_9

Saccharic acid, $C_{12} H_5 O_{11} + 5HO = C_{12} H_{10} O_{16}$ (Thaulow). This acid was designated *oxalhydric acid* by Guerin-Varry; it is a product of the action of dilute nitric acid on either cane or grape sugar. It is procured by dissolving 1 part of sugar or of gum in 2 parts of nitric acid diluted with 10 of water, and heating so long as chemical action is manifested. The acid liquid is then neutralised with carbonate of lime, and the neutral acetate of lead added to it. The saccharate of lead which falls is decomposed by sulphuretted hydrogen, and the free acid half neutralised by carbonate of potash, and crystallized as the acid saccharate of potash. The last salt is decolorized by charcoal, converted again into a salt of lead, and the acid liberated by sulphuretted hydrogen. Saccharic acid when concentrated is syrupy, colourless, sharply acid, and deposits colourless crystals, after long repose. It is soluble in alcohol in all proportions, and slightly in ether. It does not precipitate salts of barytes or lime, but produces white flocculent precipitates in barytes-water and lime-water, which are soluble in an excess of acid.

This acid is remarkable for the variety of compounds it forms with bases. It is supposed to be pentabasic, and to form 5 series of salts, according as 1 atom, 2, 3, 4, or the whole 5 atoms of water are replaced by metallic oxides; but it is possibly only tribasic, although capable of forming a subsalt with oxide of lead. Of the following salts, the composition is known

Hydrated saccharic acid	.	.	$C_{12}H_5O_{11} + 5HO$
Acid saccharate of potash	.	.	$C_{12}H_5O_{11} + \begin{smallmatrix} KO \\ 4HO \end{smallmatrix}$
Saccharate of ammonia	.	.	$C_{12}H_5O_{11} + \begin{smallmatrix} NH_4O \\ 4HO \end{smallmatrix}$
First saccharate of lead	.	.	$C_{12}H_5O_{11} + \begin{smallmatrix} 2PbO \\ 3HO \end{smallmatrix}$
Saccharate of zinc	.	.	$C_{12}H_5O_{11} + \begin{smallmatrix} 2ZnO \\ 3HO \end{smallmatrix}$
Second saccharate of lead	.	.	$C_{12}H_5O_{11} + \begin{smallmatrix} 3PbO \\ 2HO \end{smallmatrix}$
Third saccharate of lead	.	.	$C_{12}H_5O_{11} + 5PbO$

It is remarkable that hydrated saccharic acid contains the elements of 2 atoms of mucic acid; $C_{12}H_{10}O_{16} = 2(C_6H_5O_8)$; a substance produced by the same mode of oxidation of milk sugar.*

GRAPE SUGAR.

Syn. *Starch sugar, diabetic sugar, the sugar of fruits, glucose* (Dumas). The formula of crystallised grape sugar is $C_{12}H_{14}O_{14}$, but at 212^0 it fuses and loses 2 atoms of water. This is the sweet principle of raisins, figs, and of most acid fruits; it exists also in honey, and is the sugar of diabetic urine. It is also a product of the decomposition or transformation of several other substances, as of cane sugar, starch, lignin and milk sugar, when treated with dilute acids. Grape sugar is not so soluble in cold water as cane sugar, and about $2\frac{1}{2}$ times less sweet.

It is obtained from the grape, by neutralising the expressed juice with chalk, clarifying with white of egg, evaporating and setting aside to crystallize. From the urine of diabetes, by evaporating the latter to dryness in a water-bath, washing the dark crystalline mass on a filter with cold alcohol, and submitting the white residue, dissolved in water, to repeated crystallizations. But this sugar is most largely prepared from starch, and indeed, forms a considerable article of commerce. One part of potato starch is boiled with from 1-100th to 1-10th of its weight of sulphuric acid and four parts of water, for thirty-six or forty hours, the water being replaced as it evaporates. The solution

* Thaulow, sur l'Acide Saccharique, An. de Chimie, &c. lxiix, 52.

ceases to be gelatinous, and passes first into dextrin and then into sugar. Under some pressure, and at a higher temperature, the change is effected more quickly and by means of a less quantity of acid. A small quantity of oxalic acid $\frac{1}{100}$ may be substituted with advantage in this process instead of the sulphuric acid. The acid is afterwards neutralised with chalk, the solution filtered from the insoluble salt of lime, and evaporated to a syrup, which solidifies as a crystalline sugar. Starch is also converted into sugar by means of diastase. Eight parts of ground malt are infused at 158° (70° centigrade) in 400 parts of water, and then mixed with 100 parts of starch, which soon dissolves, and by continued digestion at the same temperature is entirely changed into sugar. By calculation, 100 parts of fecula, combining with the elements of four atoms of water, should produce 122.03 parts of crystallized grape sugar; De Saussure obtained 110 parts, and Brunner from 104 to 106 parts. In the transformation of starch into sugar, a variable quality of mannite is always formed at the same time, according to the observations of Fremy.

To prepare grape sugar from lignin or woody fibre, 12 parts of wood shavings or shreds of paper are gradually mixed with 5 parts of oil of vitriol diluted with 1 part of water, care being taken to avoid any rise of temperature; after twenty-four hours' digestion, the pitchy mass is dissolved in much water, and boiled for ten hours, and the acid afterwards separated as in the former process for sugar from starch.

Grape sugar does not crystallize so distinctly as cane sugar, but is obtained from its alcoholic solution in square tables or cubes, which are hard and transparent. It is soluble in $1\frac{1}{2}$ parts of cold water, and in all proportions of hot water. It dissolves less rapidly than cane sugar, and gives a more fluid syrup. In alcohol, at a low temperature, it is very sparingly soluble, but at 77° (25° cent.) it is soluble in 8 parts of alcohol of 85 per cent and in 20 parts of absolute alcohol. It fuses with loss of water at 212° , and is converted into caramel when not heated above 284° (140° cent.).

The chemical action of acids and alkalies upon grape and cane sugars are essentially different. Grape sugar dissolves in concentrated sulphuric acid, colouring it slightly yellow or brown, and forms a compound with it, the sulphosaccharic acid, while

cane sugar is carbonised in the same circumstances. On the other hand, alkalies which do not alter the colour of cane sugar, even at the boiling point, provided they are dilute, convert grape sugar, with heat, into a brown or brownish black substance. The compounds of grape sugar with barytes, lime and oxide of lead are formed with difficulty, while a crystalline compound with chloride of sodium is easily prepared.

Compounds of grape sugar.—According to the recent analyses of Erdmann and Lehman, the compound of *grape sugar and chloride of sodium* contains 2 atoms of water, which it loses at 212° . Its formula in the crystallized state is $2(C_{12}H_{12}O_{12}) + NaCl, 2HO$. This compound loses 3 atoms of water at 320° (160° cent.), according to Peligot, but then its sugar is modified. The compound of *grape sugar and oxide of lead*, precipitated on mixing the sugar with acetate of lead containing ammonia (page 594), consists, according to the analysis of Peligot, as corrected by Liebig, of $C_{12}H_{11}O_{11} + 3PbO$, or in its formation 3 atoms of water are replaced by 3 atoms of oxide of lead. The solutions of lime and barytes in grape sugar become brown, when heated.

Sulphosaccharic acid was formed by Peligot, by fusing 1 part of crystallized starch sugar by the heat of a water-bath, and then mixing the mass in small portions with concentrated sulphuric acid. The compound is then dissolved in water, and saturated with carbonate of barytes, which precipitates sulphuric acid, while the sulphosaccharate of barytes remains in solution. The acid liberated from combination is a sweet liquid, feebly acid, which forms soluble salts with almost all bases. The solution of sulphosaccharic acid is easily decomposed by evaporation, and resolved into sugar and sulphuric acid, which then precipitates barytes. Its composition has not been determined with certainty.

Sacchulmine is a substance obtained in brown, brilliant, crystalline plates, by boiling cane sugar for a very long time in very dilute sulphuric, hydrochloric or nitric acid; it is insoluble in ammonia. *Sacchulmic acid*, of which the formula is $C_{30}H_{15}O_{15}$, according to Malaguti, is formed at the same time, and many may be separated by ammonia, in which it is soluble, from sacchulmine.

Glucic acid is formed when a saturated solution of lime or

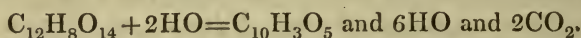
barytes, in grape sugar, is left to itself for some weeks (Peligot). The probable formula of anhydrous glucic acid is $C_{24}H_{15}O_{15}$, or it is formed from grape sugar by the loss of the elements of water. *Melassic acid* is produced by the simultaneous action of alkalies and heat upon grape sugar. With the concurrence of air and a high temperature, alkalies convert sugar into formic and sacchulmic acids.

SUGAR OF MILK OR LACTINE.

Its formula, in the crystallized state, is $C_{24}H_{24}O_{24}$, or $C_{24}H_{19}O_{19} + 5HO$; by a heat of 248° (120° cent.) it loses 2 atoms, and by 302° (150° cent.) 5 atoms of water (Berzelius). Sugar of milk is obtained by evaporating the whey of milk to crystallization, and purifying the first product by animal charcoal and a second crystallization. It forms white quadrangular prisms, terminated by four-sided pyramids, which are semi-transparent, and have the density 1.543. They are soluble in 5 or 6 parts of cold water, and in $2\frac{1}{2}$ parts of boiling water, without forming a syrup. The sweet taste of the crystals is very feeble when they are applied directly to the tongue, but that of their solution is much more distinct. Sugar of milk is unalterable in air, loses nothing at 212° , and is insoluble in alcohol and ether. Its solution dissolves hydrate of lime, and is converted by dilute mineral acids into grape sugar, assuming then the elements of 2 atoms of water. When milk is exposed to a temperature of 95° to 104° (35° to 40° cent.), it undergoes the vinous fermentation, and is found afterwards to contain alcohol, while its sugar disappears, but the latter is converted first into grape sugar, probably under the influence of the free acid which is formed and curdles the milk. Milk sugar forms two compounds with oxide of lead, of which the formulæ are $C_{24}H_{19}O_{19} + 5PbO$, and $C_{24}H_{19}O_{19} + 10PbO$ (Berzelius).

Mucic acid, $C_{12}H_8O_{14} + 2HO$ (Berzelius, Malaguti), is produced by the action of 4 parts of nitric acid, of density 1.42, diluted with 1 part of water, aided by heat, on 1 part of sugar of milk; a portion of the latter always passing at the same time into oxalic acid. It is also formed by the action of nitric acid on gum. Mucic acid is deposited on cooling, as a white crystalline powder, of which the taste is feebly acid, soluble in

6 parts of boiling water, and insoluble in alcohol. It is a bibasic acid, of which the salts of an alkaline base are soluble in water, and those which contain an alkaline earth, or the oxide of a metal proper, are insoluble. *Mucic ether*, $2C_4H_5O + C_{12}H_8O_{14}$, is solid and crystallizes in quadrilateral colourless prisms. *Modified mucic acid* is produced by boiling a concentrated solution of mucic acid, or evaporating it by heat. Its acid powers are more distinct than those of mucic acid, and it is also distinguishable from the latter by the physical properties of its salts. The modified acid is either isomeric with mucic acid, or contains the elements of an atom of water in addition (Malaguti). *Pyromucic acid*, $C_{10}H_3O_5 + HO$, is produced in the dry distillation of mucic acid, by the separation of 6 atoms of water, and 2 atoms of carbonic acid ;



It forms elongated, white and brilliant plates, which fuse at 266° (130° cent.), and volatilise without residue at a temperature a little higher. It is soluble in 26 parts of cold and in 4 parts of boiling water, dissolves easily in alcohol, and is not altered by nitric acid. It forms a class of monobasic salts, including *pyromucic ether* $C_4H_5O + C_{10}H_3O_5$, which is solid. Pyromucic ether absorbs 4 atoms of chlorine gas and becomes liquid, without the liberation of any hydrochloric acid, forming a compound, which Malaguti names *chloropyromucic ether*, $C_{14}H_8Cl_4O_6$, but of which the true constitution is uncertain.

MUSHROOM SUGAR.

This sugar, of which the formula is $C_{12}H_{13}O_{13}$, according to an analysis by MM. Liebig and Pelouze, was obtained by M. Wiggers by treating the tincture of the ergot of rye by water. It crystallizes, and is soluble in water and alcohol, but not in ether. Mushroom sugar is also fermentable by yeast, and diffuses the odour of caramel when carbonised by a high temperature. This sugar does not throw down sub-oxide of copper from a boiling solution of the acetate, the only property by which this sugar is distinguished from the ordinary species.

INSIPID SUGAR.

A species of sugar was obtained by Thenard, from the urine of diabetes insipidus, and subsequently by Bouchardat from the same source, which was insipid, or only faintly sweet. It was fermentable by yeast, and was converted by dilute sulphuric acid into the sugar of grapes.*

LIQUORICE SUGAR.

The inspissated juice of the root of the *Glycyrrhiza glabra*, contains a species of unfermentable sugar, which is obtained by clarifying the juice with albumen, and precipitating the sugar with sulphuric acid, washing the precipitate with water, dissolving it in alcohol, which leaves undissolved some albumen, and then decomposing the sulphate of liquorice sugar by carbonate of potash. After evaporation, the sugar remains as a yellow translucent mass, cracked in all directions, and easily detached from the vessel in which it was evaporated. Liquorice sugar possesses the property of forming soluble or sparingly soluble compounds with both the mineral and vegetable acids. It also combines with bases.

MANNA SUGAR, OR MANNITE.

$C_6H_7O_6$, according to the analyses of Oppermann and of Liebig. Manna is in oblong globules or masses, of a yellowish white colour, and is an exudation from various trees, principally the *Fraxinus ornus*, a species of ash, and the *Eucalyptus mannifera* of New South Wales. It exists also in the juices exuded by many cherry and plum trees, in various kinds of mushrooms, and in some roots, such as that of celery. It is composed chiefly of manna sugar, which may be prepared by dissolving the manna of the shops in boiling alcohol, and allowing the solution to cool, and is obtained perfectly pure by repeated crystallizations. Mannite crystallizes in slender, colourless, four-sided prisms, of a silky lustre. It has a slightly sweet taste, and is very soluble in water; its solution is not fermentable. Mannite is anhydrous, and may be fused by heat without loss of weight.

* Thenard, *Traité de Chimie*, IV. 351.

Its solution dissolves oxide of lead. Nitric acid converts mannite into oxalic and saccharic acids, and not into mucic acid.

Mannite is also one of the products of the viscous fermentation of cane and grape sugar, which will be afterwards described.

GUM.

Its formula is $C_{12}H_{11}O_{11}$; it loses an atom of water at 266° (130° cent.), but is then essentially altered. Gum is a principle of constant occurrence in the juices of plants, and exuding from the bark of trees, collects into drops, which are distinguishable from resin by being soluble in water and insoluble in alcohol. All the varieties of gum may be referred to two species, of which gum-arabic (the produce of the acacia vera), and gum-tragacanth are the types. The first is slowly soluble in cold water, the last does not dissolve in water, but swells up into a mucilaginous mass, which, when boiled, gradually acquires the appearance of ordinary gum. The solution of gum, known as mucilage, is a thick, adhesive, insipid liquid, from which the gum is thrown down by alcohol. Gum is precipitated by sub-acetate of lead, as a white mass, insoluble in water. It is destroyed by the strong acids; nitric acid converts it into mucic acid.

LIGNIN.

The formula of lignin, dried between 300° and 350° is $C_{12}H_8O_8$ (Prout). The basis of woody fibre is aptly so named. It constitutes about 95 per cent of baked wood, and is the most durable product of vegetation. Pure lignin is obtained by treating the sawings of wood, paper, or the fibre of lint and cotton, successively with ether, alcohol, water, a diluted acid, and a diluted caustic alkali, to dissolve all the matters soluble in these menstrua. Wood contains in its vessels the various constituents of the sap, of which the colouring principle attaches itself to the lignin on evaporation, by a chemical affinity, such as we avail ourselves of in dyeing vegetable fibre. It has been observed by Hartig that the pores of wood also contain a certain quantity of starch, in spherical grains of a grey colour, of which from one-fourth to one-fifth of the weight of the wood may be obtained by mechanical means. The lignin of wood consists

according to M. Payen, of two organic principles, which he has succeeded in separating; one is the primitive tissue, composing the vessels of the wood, which is isomeric with starch, $C_{12}H_{10}O_{10}$, and is named by him *cellulose*; the other fills the cells, and constitutes the true ligneous matter. M. Payen obtained cellulose by the action on the sawings of beech-wood of several times its weight of the most concentrated nitric acid, which leaves that principle, while it dissolves the lignin. Cellulose is dissolved by concentrated sulphuric acid, without blackening, and is then converted into dextrin. The true lignin of lint, hemp, straw, and linen cloth, was found by Payen to be $C_{35}H_{24}O_{20}$. Oak-wood, by the analysis of Gay-Lussac and Thenard, is $C_{36}H_{22}O_{22}$. Hemp, straw, etc. mixed cautiously with concentrated sulphuric acid, so as to prevent elevation of temperature, form, besides dextrine, a *lignin-sulphuric acid*, analogous to benzo-sulphuric acid, which forms soluble salts with barytes and oxide of lead. The dextrin formed when lignin is dissolved in sulphuric acid, is converted by dilution and boiling, into starch sugar. Sawdust, gum and starch dissolve in the most highly concentrated nitric acid (page 295), without decomposition of the acid, and if immediately diluted with water, give a white pulverulent neutral substance, insoluble in water, which contains the elements of nitric acid and is highly combustible (Robiquet).

Lignin combines with several neutral salts, such as chloride of mercury, sulphate of copper, and acetate of iron, with all of which, particularly the first, wood is impregnated, in order to preserve it from *dry rot*, a species of decay to which wood is subject. The wood loses all its cohesion, and becomes friable when affected by dry rot, and fungi generally appear upon it, but the first destructive change is probably of a chemical kind allied to the action of fermentation. Dr. Boucherie has found that wood may be completely charged with solutions of salts for its preservation, by aspiration from the roots or base of the trunk of the tree, shortly after it is cut down, and has made many other new observations on the subject.*

Suberic acid, $HO + C_8H_6O_3$, is formed among other products by the action of moderately concentrated nitric acid, with heat,

* Annales de Chim. etc. lxxiv. 113.

upon barks, but more particularly cork. It is produced, likewise, from stearic and oleic acids in the same manner. Suberic acid is deposited from a saturated hot solution in water, as a white earthy powder, slightly sour, which is fusible and distils over like an oil, fixes on cooling, and is crystalline. It is soluble in alcohol and ether.

SECTION II.

PRODUCTS OF THE FERMENTATION OF SUGAR.

ETHYL SERIES OF COMPOUNDS.

Ethyl, $C_4H_5=E$, a hypothetical radical, existing in ether and its compounds; ether being the oxide of ethyl, and alcohol the hydrated oxide of ethyl. Ethyl has not been isolated.

HYDRATED OXIDE OF ETHYL, OR ALCOHOL.

Its formula is $C_4H_5O + HO = EO + HO$. Alcohol can be obtained only in one way, namely by the fermentation of sugar, and perhaps immediately from grape or starch sugar only. This fermentation is determined by the addition of yeast to a solution of sugar kept between 70^0 and 80^0 , when a new distribution of the elements of the latter takes place, so as to form alcohol and carbonic acid; one atom of starch sugar $C_{12}H_{12}O_{12}$ being converted into two atoms of alcohol $2 (C_4H_5O + HO)$, and four atoms of carbonic acid $4CO_2$.

Two atoms of alcohol . . .	C_8	H_{12}	O_4
Four atoms of carbonic acid .	C_4		O_8
One atom of starch sugar .	C_{12}	H_{12}	O_{12}

The juices of all plants which naturally contain sugar, possess, likewise, a substance which by exposure to air, becomes a ferment and converts their sugar into alcohol and carbonic acid. Hence all saccharine vegetable juices, such as that of the grape, of sugar-cane, and of beet-root, run quickly into fermentation after expression.

Alcohol is obtained by distillation from all liquids which have undergone the vinous fermentation, but diluted with a large

quantity of water. The density of the distilled liquid diminishes with the proportion of alcohol, and tables have been constructed by which from its density the per-centage of alcohol in the liquid may be ascertained. Ordinary spirits have a specific gravity from 0.910 to 0.915, which corresponds with from 50 to 52 per cent. of alcohol. The same distilled afford a spirit of density from 0.890 to 0.880, at 60°, known as *spirits of wine*, containing from 62 to 67 per cent of alcohol; which again may be brought, by a second distillation, to from 0.843 to 0.835, known as *rectified spirits*, and these contain from 82 to 85 per cent. of alcohol.* To obtain alcohol free from water, or *absolute alcohol*, rectified spirits may be poured into a retort over their weight of anhydrous lime, in fine powder, either fresh quick-lime finely pulverised, or better lime that has been slaked and afterwards heated recently to redness, allowed to digest together for twenty-four hours, and the spirit afterwards slowly distilled by the heat of a water-bath. It then has a specific gravity of 0.7947 at 59° (15° cent.), and from 0.792 to 0.791 at 68° (20° cent.). The *proof spirits* of the excise, upon which the duty per gallon is levied in this country, is of density 0.918633; and by the expression that a spirit is any number, say *ten*, over *proof*, is meant that 100 gallons of the spirit would stand the addition of ten gallons of water to reduce it to proof strength, or it would form 110 gallons of proof spirit; while *ten under proof*, means that ten gallons of water must be taken from 100 gallons of the spirit to raise it to proof, or that 100 gallons of it contain only 90 gallons of proof spirit. The proof spirit of the pharmacopœia (*spiritus tenuior*) is directed to be of sp. gr. 0.930. When obtained from grain, alcohol always contains a small quantity of a particular oil, from which it is most easily purified on the small scale by distilling it from caustic potash, or filtering it, when in a large quantity, through a bed of recently prepared wood charcoal, roughly pounded.

Alcohol has never been frozen. By evaporating the compound of solid carbonic acid and ether, in the vacuum of an air-pump, Dr. Mitchell has produced the greatest depression of temperature hitherto attained. Alcohol of specific gravity 0.798, was observed by him to become oily and adhesive at—130°;

* Table of the Density of Alcohol, by M. Lowitz, see Appendix.

by a greater cold it became still thicker, and at -146° flowed like melted wax. Alcohol of 0.820 froze easily; ether underwent no change by the lowest of these temperatures.*

Alcohol boils at 173° (barometer 29.5 inches), and at higher temperatures, in proportion as it is diluted with water. It is remarkable, however, that the boiling point of a mixture of alcohol and water rises with the quantity of water to a certain point; alcohol of 96 to 99 per cent boiling at a somewhat lower temperature than absolute alcohol. In consequence of this, alcohol of density 0.800 is increased in strength by boiling it: and hence also, in the preparation of absolute alcohol, the first portions contain always a little more water than those which follow. Alcohol has an agreeable penetrating odour, and is the intoxicating principle of all spirituous liquors. The density of its vapour, according to Gay-Lussac, is 1613, referred to air as 1000; it contains eight volumes of carbon vapour, twelve volumes of hydrogen, and two volumes of oxygen condensed into four volumes, its combining measure, which gives the theoretical density 1601. Alcohol is highly combustible, and burns with a flame that is nearly colourless and free from smoke; the only products of its perfect combustion are water and carbonic acid.

Alcohol has a great attraction for water, which when anhydrous, alcohol attracts rapidly from the air. It also withdraws water from animal substances, and thus preserves them. When mixed with water, a very sensible evolution of heat occurs, and always a diminution of bulk and increase of density, when water and absolute alcohol are mixed in any proportions, although on adding water to alcohol, already considerably diluted, an apparent expansion may be observed. The greatest contraction occurs on mixing 1 atom of alcohol with 6 atoms of water, when a definite hydrate is certainly formed; 100 volumes of this mixture contain 53.939 volumes of alcohol, and 49.836 volumes of water; consequently, 103.775 volumes are reduced to 100; its density is 0.927 at 59° .†

Alcohol dissolves most of the gases, and several of them in a

* Liebig's *Annalen*, vol. 37, p. 354; from Silliman's *American Journal of Science*.

† Rudberg, *Annales de Chim.* etc. *xlvi*, 33.

larger proportion than water, such as oxygen, nitrous oxide, carbonic acid, and phosphuretted hydrogen. It dissolves the hydrates of potash and soda, ammonia, the alkaline sulphurets, likewise all the deliquescent inorganic salts, except carbonate of potash, but none of the salts which are insoluble or sparingly soluble in water, nor efflorescent salts. It dissolves many vegetable principles, such as sugar, resins, essential oils, soap, castor oil, ethers, alkalies, most acids, &c. It does not dissolve the fats and fixed oils. Alcohol forms crystalline compounds with several of the salts it dissolves, particularly chloride of calcium, ($\text{CaCl} + 2\text{C}_4\text{H}_6\text{O}_2$), nitrates of lime and magnesia, chloride of zinc, and chloride of manganese. These compounds are named *alcoates*, and correspond with hydrates, but are much less stable. Many solutions made by alcohol, or *tinctures*, are used in medicine.

Absolute alcohol dissolves 1-240th of phosphorus, and 1-200th of sulphur. It is decomposed by potassium or sodium, with the evolution of hydrogen gas, and a crystallizable compound is formed of the remaining elements of the alcohol with the metal, or perhaps of ether with the oxide of the metal. This substance is decomposed by water. Oxygen acids decompose alcohol; as they do a hydrated metallic oxide, uniting directly with the ether it contains, and forming acid salts of that base; while a hydracid acts upon the ether of the alcohol as it does upon a metallic oxide, forming water, and a haloid compound of the radical of the hydracid with ethyl.

OXIDE OF ETHYL, OR ETHER.

Formula: $\text{C}_4\text{H}_5\text{O} = \text{EO}$; distinguished also as *sulphuric ether*, from the mode of preparing it. This liquid is the product of a remarkable decomposition of alcohol by sulphuric, phosphoric and arsenic acids, and is also formed by the action upon alcohol of the fluoride of boron, the chloride of zinc, the chloride of tin, and some other chlorides. All these agents have a great affinity for water, and might be supposed to convert alcohol into ether by simply combining with the water which the former is supposed to contain, but the close examination which the process of etherification has received from chemists, proves that its rationale is by no means so simple. Reserving the theory of

ether till that of sulpho-vinic acid is considered, I shall at present describe the process for ether.

Ether is evolved when alcohol and oil of vitriol are heated together, and may be obtained by mixing and distilling in a glass retort equal weights of these materials, due attention being paid to the condensation of the product, which is volatile, by keeping the receiver very cold. But as the power of the acid to decompose alcohol is not exhausted in this process, it is found advantageous to make additions of alcohol to the remaining acid, or to introduce the latter in a continued stream. The following is a *continuous process* for ether, first proposed by M. Mitscherlich, as it is given by M. Liebig. Alcohol is employed of density 0.822, or of 90 per cent. which may be obtained by digesting proof spirits upon an equal weight of well dried carbonate of potash (free from caustic potash), when two liquids are formed, the upper alcohol of the strength mentioned, which may be drawn off for use, and the lower, a solution of carbonate of potash in water. Five parts, by weight, of this alcohol are mixed with nine parts of oil of vitriol, in a copper or cast iron vessel, surrounded by cold water, and the mixture afterwards introduced into a tubulated glass retort, which the mixture should fill one half, or even a little more. The distillation is best conducted by the heat of a sand-pot, in which the retort should not be deeply sunk, and commences at a gentle heat; when the temperature increases too briskly, the fire should be withdrawn. A glass tube is fixed by a cork in the tubulure of the retort, of which the extremity within the retort is drawn out into a point, having an opening about one line in diameter, and dips one inch in the liquid. Without the retort, the same tube is bent at a right angle, and may extend horizontally for two or three feet; it communicates with a reservoir of alcohol by means of a metallic tube and stop-cock, by which the flow of the alcohol is regulated. The latter should be supplied so as to keep the liquid in the retort at its original level, at which a mark should be placed for that purpose. To condense the ether which distils over, the beak of the retort is connected with Liebig's tube condenser, charged with the coldest water. A leaden alembic is used when ether is prepared on a large scale. It is said that when operation is well directed, nothing is formed but ether and water; the same sulphuric acid may

also be used indefinitely for the preparation of ether without sensibly diminishing, the ether and water into which the alcohol is resolved, coming off entirely, and leaving none of its elements with the acid.

To obtain the ether perfectly free from alcohol and other impurities, the crude product may be mixed with some milk of lime and an equal volume of water, the lighter liquid drawn off, and allowed to digest for several days upon chloride of calcium, or quicklime; and finally be rectified from the same substances. The last product has a specific gravity between 0.720 and 0.725.

Ether is a light, transparent, highly limpid, fragrant and volatile liquid, having a sharp aromatic taste, and which when swallowed or inhaled in the form of vapour, acts as a powerful stimulant. Its density is 0.715 at 68° , and 0.724 at 54° , by Gay-Lussac's observations. It boils between 96° and 98° ($26^{\circ}.5$ cent. Gay-Lussac); evaporates rapidly at ordinary temperatures, and produces great cold by its evaporation. It is very combustible, and a mixture of its vapour with air or oxygen is explosive in a high degree; hence it must always be distilled with caution. Ether, unlike alcohol, burns with a white flame; it is converted into water and carbonic acid. When a spiral coil of platinum wire, heated red-hot, is suspended in the vapour of ether, the latter burns without flame, and produces a very acrid vapour, which when condensed has been found to contain acetic, formic and aldehydic acids. When transmitted through a red hot tube, ether is decomposed into aldehyde, olefiant gas, and the gas of marshes.

Ether mixes with alcohol in all proportions, but may be separated completely from the latter by agitation with twice its bulk of water, which takes up the alcohol while the ether floats on its surface. One part of ether dissolves in 10 parts of water, while 36 parts of ether dissolve 1 of water. Its solvent powers are much less extensive than those of alcohol. Ether dissolves 1-80th of sulphur, and 1-37th of phosphorus, and also iodine and bromine in large quantity, but is soon decomposed by them. It dissolves also a considerable number of chlorides, such as that of mercury, of zinc, and gold. Ether dissolves also several organic acids, such as the acetic, gallic, benzoic, oleic and stearic acids, also the essential oils, fats, wax, and certain resins. Certain vegetable bases are also soluble in ether, while others are not.

The vapour of ether is very heavy, its density being 2586 (Gay-Lussac); it contains 8 volumes of carbon vapour, 10 volumes of hydrogen, and 1 volume of oxygen, condensed into 2 volumes, which form its combining measure, and give as its theoretical density 2583.

Ether left a long time in contact with water, combines with it and forms alcohol. It combines with acids, and forms both neutral and acid salts; the first class of salts are the compound ethers, and the last bear the name of vinic acids.

CHLORIDE OF ETHYL, OR HYDROCLORIC ETHER.

Its formula is $C_4H_5Cl = ECl$. To prepare this ether, alcohol is saturated with hydrochloric acid gas, and the solution distilled by a water-bath heat; the product is conducted into a bottle containing some water and surrounded by water at the temperature of 70° or 80° , and thence into another receiver surrounded by ice. To free it from water and alcohol, the product is digested with chloride of calcium in a bottle surrounded by ice. The liquid is decanted, after twenty-four hours, into phials, with well ground stoppers, which are kept inverted.

Hydrochloric ether is a highly volatile liquid, boiling at 52° , of a penetrating aromatic and slightly alliaceous odour. Its density is 0.874 at 41° , it is neutral to test paper, dissolves in twenty-four parts of water, and gives a solution that is not precipitated by nitrate of silver. When treated with chlorine, it gives hydrochloric acid, and a series of compounds to which reference has already been made (page 718).

Bromide of ethyl, $C_4H_5Br = EBr$, was discovered by Serullas, and is formed by distilling a mixture of 1 part of bromine, 4 of alcohol, and 1-8th of phosphorus. It is a colourless and very volatile liquid, denser than water.

Iodide of ethyl, $C_4H_5I = EI$, may be obtained by distilling alcohol, saturated with hydriodic acid gas. It is a colourless liquid, of density 1.9206, which boils at 161° . (71° . 5 cent.)

Sulphuret of ethyl, $C_4H_5S = ES$, is formed by transmitting the vapour of hydrochloric ether through the proto-sulphuret of potassium; chloride of potassium precipitates, the sulphuret of ethyl is dissolved by the liquid, or distils over if the latter is kept warm. It is a colourless liquid, of a disagreeable allia-

ceous odour, boiling at $163^{\circ}.4$ (73° cent.), and of which the density is 0.825 at 68° .*

HYDROSULPHURET OF THE SULPHURET OF ETHYL, OR MERCAPTAN.

Its formula is $C_4H_5S + HS = ES + HS$; or it is alcohol of which the oxygen is replaced by sulphur. This curious compound, of which we owe the discovery to Zeise, may be prepared like the preceding compound, by transmitting the vapour of hydrochloric ether through a strong solution of potash, previously saturated with sulphuretted hydrogen gas, or hydrosulphuret of sulphuret of potassium, $KS + HS$; but a preferable process is to distil a strong solution of the sulphate of oxide of ethyl and lime, of density 1.28, mixed with a solution of potash of the same density, previously saturated with sulphuretted hydrogen gas.

KS, SH and $(EO + CaO + 2SO_3) = ES + HS$ and $KO + SO_3$ and $CaO + SO_3$.

The product must be received in a cool receiver. It contains an excess of sulphuretted hydrogen, alcohol, and water, from which it may be purified by submitting it to a second distillation from a small quantity of red oxide of mercury, and digesting it afterwards with chloride of calcium.

Mercaptan is a colourless liquid, highly fluid like ether, having a most penetrating and insupportable garlic odour; its boiling point is about 100° , according to my own observation, and the density is said to be 0.835 at 70° , and 0.842 at 59° . It is miscible with alcohol and ether, but not with water, in which it is very slightly soluble. The sulphuretted hydrogen of mercaptan acts powerfully on metallic oxides, water being formed, and a sulphuret of the metal, which last remains in combination with the sulphuret of ethyl, thus forming a class of sulphur salts. The oxide of mercury is instantly converted by mercaptan into a compound of this class, $C_4H_5S + HgS$,† the *mercaptide of mercury*, which is a white crystalline mass, soft to the touch, without odour, insoluble in water, and fusible like wax by 185° (85° cent.). This mercaptide, when distilled, leaves cinnabar, and affords a volatile liquid, which has not been

* Regnault, An. de Ch. etc. lxxi, 387.

† Hence the name mercaptan, from *mercurium captans*.

examined. The oxide of gold is also strongly acted on by mercaptan, but other metallic oxides are less affected in proportion as they approach to alkaline bases. Thus the hydrates of potash and soda have no sensible action on mercaptan.

By contact with nitric acid, mercaptan is converted, by a gentle heat, into a new acid, which contains sulphuret of ethyl and the elements of sulphuric acid, $C_4H_5S_2O_2$. (Lœwig, Kopp).

Bisulphuret of ethyl, $C_4H_5S_2=ES_2$, is a transparent oily liquid, boiling at 123.8° (51° cent.), obtained by distilling a mixture of the double sulphate of ethyl and potash and the persulphuret of potassium. It is decomposed by caustic potash and by nitric acid (Zeise, Pyrame Morin).

Seleniuret of ethyl, is obtained, according to Lœwig, in the same way as the sulphuret, substituting in the process seleniuret of potassium for the sulphuret of potassium.

Telluret of ethyl, obtained also by a similar process, using the telluret of potassium; a very volatile liquid, of a deep orange colour (Wœhler).

Cyanide of ethyl, hydrocyanic ether, $C_4H_5 + NC_2 = ECy$, obtained by Pelouze by exposing a dry mixture of sulphate of ethyl and potash to a gentle heat, which is gradually increased. It is a colourless liquid, with an insupportable odour of garlic, boiling at 179.6° (82° cent.), and of which the density is 0.7. *Sulphocyanide of ethyl* has also been formed by distilling a mixture of sulphocyanide of potassium, alcohol and sulphuric acid. It is an oily, very dense liquid.

SALTS OF OXIDE OF ETHYL, OR SALTS OF ETHER.

Ether does not combine directly with acids, but these salts are obtained by the action of acids upon alcohol (hydrate of ether). The neutral salts of ether are distinguished from inorganic salts by the circumstance that neither the acid nor oxide of ethyl can be replaced by double decomposition, at the ordinary temperature, by another acid or base, when the salt of it is mixed with another salt; the alcoholic solution of the oxalate of ether, for instance, not being precipitated by an alcoholic solution of chloride of calcium. These salts are decomposed by the alkaline hydrates, particularly when assisted by heat, their base attaching itself to the water of the alkaline hydrate, and coming off as alcohol, while their acid unites with the alkali. Several of these

neutral salts are only partially decomposed by alkalies and metallic oxides, a neutral double salt being formed, in which the acid is united with equal proportions of oxide of ethyl and metallic oxide. The latter can again be removed by a stronger acid for which it has an affinity, and then an acid double salt is formed, in which the ethyl is combined with a salt of water. The metallic oxide of the neutral double salts can also be replaced by another metallic oxide, but the acid of the double salt is not affected by its usual precipitants, the sulphate of ethyl and potash, for instance, not being precipitated by chloride of barium.

The acid salts of oxide of ethyl are not crystallizable, a concentrated solution has a certain degree of stability, and may be heated to 212° , but a dilute solution decomposes spontaneously at the temperature of the air, and more rapidly when heated, with the formation of alcohol and a hydrate of the acid. Some of them, of which the hydrate is but slightly volatile, such as the acid sulphate of ether, are decomposed at a higher temperature into ether which escapes and acid which remains in the state of hydrate.

The neutral salts of ethyl are generally derived from the acid sulphate of ethyl. When to a highly concentrated solution of the latter, solutions of other acids are added, it usually happens that the latter assume the oxide of ethyl to form neutral salts, and leave behind the hydrate of sulphuric acid; the mucate, oleate and stearate of ethyl are formed in this way. Or when to a similar solution of the acid sulphate of ethyl salts are added, of which the acids are volatile and form volatile compounds with oxide of ethyl, the sulphuric acid unites with the base of the other salt, while the volatile acid combines with oxide of ethyl, and distils over with the latter.

ACID SULPHATE OF OXIDE OF ETHYL, OR SULPHATE OF OXIDE OF ETHYL AND WATER.

Syn. *Etherosulphuric acid*, *sulphethylic acid* (Mitscherlich), *sulphovinic acid*; $\text{EO}, \text{SO}_3 + \text{HO}, \text{SO}_3$.

The neutral sulphate of ethyl has not yet been formed.

The acid sulphate of ethyl may be formed directly by transmitting the vapour of ether through the hydrate of sulphuric acid so long as it is dissolved. On afterwards diluting that

liquid with water, part of the ether separates in a free state, and part remains in combination with the acid.

The same compound, however, is obtained from the action of sulphuric acid on alcohol, a chemical action which cannot yet be said to be fully explained, although it has been the subject of much research. There are two steps in this action: 1. the production of sulphovinic acid, and 2. the liberation of ether.

1. *Formation of sulphovinic acid.*—Equal weights of strong alcohol and oil of vitriol heated together to the boiling point of the mixture, and saturated at that temperature with milk of lime, give the sulphovinate of lime, or sulphate of ethyl and lime, which is soluble and may be separated by filtration from a considerable quantity of insoluble sulphate of lime, which is always formed at the same time. It is observed that the cooling and the dilution of the mixture of alcohol and sulphuric acid, before saturation, diminishes the proportion of sulphovinic acid, or of sulphovinate of lime formed, by causing a reproduction of alcohol. Even when the sulphuric acid is in great excess, a considerable proportion of alcohol, often nearly the half of it, escapes decomposition, or is not found in the sulphovinic acid when neutralised. That the whole alcohol, however, is at first converted into sulphovinic acid appears from the circumstance that the mixture is not decomposed by a current of dry chlorine, no hydrochloric being formed, a property of sulphovinates, which undergo no modification by the action of chlorine, while free alcohol is immediately decomposed into hydrochloric acid and other chloruretted products. A mixture of 100 parts of oil of vitriol, 48 parts of alcohol, and 18.5 parts of water, which contains the elements of 2 atoms of sulphuric acid, 1 atom of ether, and 6 atoms of water, boils at 284° (140° cent.), and is not affected by chlorine; it may be represented as $(\text{EO}, \text{SO}_3 + \text{HO}, \text{SO}_3) + 5\text{HO}$.

The protohydrate of sulphuric acid, diluted with 55 per cent. of water, or $\text{HO}, \text{SO}_3 + 3\text{HO}$, does not decompose alcohol at the ordinary temperature, but the reaction occurs when the mixture is boiled.

It is observed by Mitscherlich that in the formation of sulphovinic acid, there is only a feeble disengagement of heat. If to two parts of alcohol, one part of sulphuric acid and then one part of water be added, the temperature of the mixture rises to 518° (70° cent.); about half of the alcohol being converted into

sulphovinic acid. While if to one part of sulphuric acid, one part of water be first added, and then two parts of alcohol, the temperature rises to 154.4° (86° cent.), or nearly as high, although in the last case no sulphovinic acid is formed. Consequently the heat evolved when sulphuric acid unites with oxide of ethyl is scarcely superior to that liberated when the protohydrate of sulphuric acid unites with more water.*

2. *Formation of ether.*—A mixture of 9 parts of hydrated sulphuric acid and 5 parts of alcohol of 85 per cent which is heated to the boiling point for ether, contains the elements exactly of 1 atom of the acid sulphate of ether, and 3 atoms of water, or $(EO,SO_3 + HO,SO_3) + 3HO$. When this mixture is heated above 284° , the acid sulphate of oxide of ethyl is decomposed into ether and water, which distil over very nearly if not exactly in the proportions in which they exist in alcohol. The escape of ether from this mixture is not promoted by the addition of strong sulphuric acid to it, but, on the contrary, retarded, and then requires a higher temperature. On the other hand, more alcohol added to the mixture distils off undecomposed in the anhydrous state. The water present in the ether mixture is necessary, and must act as a stronger base, displacing the oxide of ethyl in combination with the acid, and liberating it as ether (page 188). Water may even displace so strong a base as ammonia, when assisted by the volatility of the latter; a solution of the neutral sulphate of ammonia becoming acid when boiled for some time, from the escape of ammonia (Rose). The addition, however, of more water to the ether mixture above, so as to lower its boiling point below 258.8° (126° cent.), occasions the destruction of the sulphovinic acid, and then nothing but alcohol distils over.

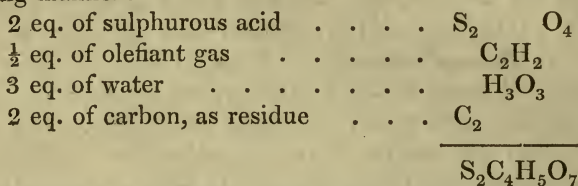
It was observed by Rose that ether begins to be slowly evolved from the ether mixture, at a temperature scarcely amounting to 212° ; the ether is nearly pure, the water of the alcohol being retained at that temperature by the sulphuric acid.† Liebig finds that on directing a current of dry air through the ether mixture heated to 284° , the point of ebullition falls to 273.2° (134° cent.), and on examining what was carried away by the

* L'Institut, No. 390, page 206; 17 Juin, 1841; where etherification and other theoretical questions are discussed by M. Mitscherlich.

† H. Rose on Etherification, Taylor's Scientific Memoirs, vol. ii.

air, it was found to be nothing but alcohol.* The evolution of ether does not indeed proceed well, unless with a regular ebullition of the liquid.

When the ether mixture contains a great excess of sulphuric acid, the decomposition of the sulphate of oxide of ethyl does not take place till the temperature rises to 320° (160° cent.), and then a variety of products are evolved, which Liebig refers to the re-action of the elements of sulphuric acid themselves upon oxide of ethyl. He supposes the elements of 1 atom of the acid sulphate of oxide of ethyl to divide themselves in the following manner :



This appears to represent pretty well the decomposition by which olefiant gas is usually obtained (page 426) ; but that gas may be obtained, according to Mitscherlich, accompanied by nothing but water, when sulphuric acid is diluted with water so as to boil at 320° , and the vapour of alcohol containing 20 per cent of water (density 0.844) is sent through it. After a part of the water is expelled by the heat, bubbles of olefiant gas appear in all parts of the liquid. The gas is accompanied by very little ether, and by almost no acid body ; and the liquid, even after it has produced a cubic foot of olefiant gas remains colourless, without any deposit of carbon. The other substances obtained in the ordinary preparation of olefiant gas, Mitscherlich considers as secondary products, which only begin to be formed when with alcohol of 80 per cent a temperature is employed of 338° (170° cent.).

In the ordinary decomposition of alcohol for olefiant gas, there is also formed a small quantity of the double sulphate of oxide of ethyl and etherole (oil of wine). The carbonaceous residue has also been shown not to be pure carbon, but a compound substance, and named *Thiomelanic acid* by Erdman. Its composition in its potash salt is $C_{80}H_{24}S_3O_{20} + 2KO$.

The solution of the acid sulphate of oxide of ethyl is a liquid of a very sour taste ; when diluted it cannot be concentrated by

* *Traité de Chimie Organique*, tome i, page 334.

evaporation at any temperature without decomposition. It is obtained in a state of perfect purity by heating slightly the sulphate of ethyl and etherole in contact with 4 parts of water; the etherole (light oil of wine) separates and comes to the surface, while the acid sulphate of ethyl dissolves in the water. It forms a great number of double salts with bases, which to 2 atoms of sulphuric acid contain 1 atom of oxide of ethyl, and 1 atom of the base added. They are soluble in water, and in alcohol which is not anhydrous; their sulphuric acid cannot be detected by the usual re-agents, but on boiling their solution with a few drops of hydrochloric acid, alcohol is disengaged, and thereafter the presence of sulphuric acid can easily be detected in the residue. They are not decomposed by a current of gaseous chlorine; the potash and soda salts are not decomposed when boiled with an excess of these alkalies; the barytic salt distilled with sulphuric acid containing 4 atoms of water gives a mixture of ether and alcohol; concentrated solutions of all of them are gradually decomposed by ebullition. When a sulphovinate is submitted to dry distillation with hydrate of lime or barytes, it is converted into a neutral sulphate and alcohol.

The sulphovinate of potash is the only anhydrous salt, all the others contain water of crystallization, which they generally lose when dried in vacuo at the ordinary temperature. The salts of potash, soda, and ammonia are prepared by precipitating the double sulphate of ethyl and lime or the salt of barytes, by the alkaline carbonates; the double sulphate of ethyl and magnesia or manganese, by decomposing the double sulphate of ethyl and barytes, by means of soluble sulphates.

These salts have all more the character of a bibasic salt, than of a double sulphate or compound of two monobasic sulphates, and may therefore be represented as containing a sulphuric acid of double atom S_2O_6 , which is bibasic, and is united at once with oxide of ethyl and another base, of which the last only can be displaced by other bases. They resemble the bibasic fulminate of silver, in which one atom only of base can be displaced by another base.

Sulphate of oxide of ethyl and potash, $KO,EO + S_2O_6$, crystallizes in colourless plates like chlorate of potash, which have a saline and sweetish taste; is persistent in air, soluble in an equal

weight of water, also in dilute alcohol, but insoluble in anhydrous alcohol and ether; above 212° it undergoes decomposition without entering into fusion.

Sulphate of oxide of ethyl, and barytes, $\text{BaO}, \text{EO} + \text{S}_2\text{O}_6 + 2\text{HO}$, crystallizes in plates or rhomboidal prisms, persistent in air, and having a very acid taste.

Sulphate of oxide of ethyl, and lime, $\text{CaO}, \text{EO} + \text{S}_2\text{O}_6 + 2\text{HO}$. Five parts of this salt dissolve in 4 parts of water at 62.6 (17° cent.); it is also soluble in alcohol with the aid of heat.

Sulphate of oxide of ethyl, and oxide of lead, $\text{PbO}, \text{EO} + \text{S}_2\text{O}_6 + 2\text{HO}$, crystallizes in large transparent tables, very soluble both in water and alcohol, and having an acid re-action. It slowly undergoes spontaneous decomposition, and becomes viscid from the formation of oil of wine. It dissolves an additional atom of oxide of lead, and becomes a *basic salt*, which becomes a white mass, and is very soluble.

Acid phosphate of oxide of ethyl, phosphovinic acid, $2\text{HO}, \text{EO} + \text{PO}_5$, is formed on mixing alcohol with a concentrated solution of phosphoric acid, with the evolution of much heat; if the phosphoric acid is diluted so that its density does not exceed 1.2, it is not in a state to decompose alcohol. Phosphovinic acid is a colourless, syrupy liquid, of an acrid and very acid taste, more stable than sulphovinic acid, as it may be boiled without decomposition, even when diluted. At a higher temperature it is decomposed, giving first ether and alcohol, then inflammable gases and a carbonaceous residue. When phosphovinic acid is treated with metallic oxides, the two atoms of basic water which it contains are separated and replaced by fixed base, while the oxide of ethyl remains, a tribasic class of salts being formed like the ordinary phosphates. The formula of the *phosphate of ethyl and barytes* is $2\text{BaO}, \text{EO} + \text{PO}_5 + 12\text{HO}$. The compounds of pyrophosphoric acid and metaphosphoric acid with oxide of ethyl have not yet been obtained (Pelouze).

Arseniate of oxide of ethyl, arseniovinic acid, $\text{HO}, 2\text{EO} + \text{AsO}_5$, contains 2 atoms of oxide of ethyl and 1 atom of basic water, which last may be replaced by fixed bases (D'Arcet).

Nitrite of oxide of ethyl, nitrous ether, $\text{C}_4\text{H}_5\text{O} + \text{NO}_3 = \text{EO}, \text{NO}_3$. Nitric acid decomposes alcohol without combining with it. This ether may be obtained, however, by distilling 3 parts of strong alcohol with 2 parts of nitric acid of density 1.3, applying occasionally a very gentle heat, and condensing in a receiver

surrounded by ice. But as prepared with nitric acid, by this and other processes, nitrous ether always contains aldehyde, a product of the oxidation of alcohol. M. Liebig recommends as the best process for nitrous ether, to transmit a current of nitrous acid vapour, obtained by heating on a water-bath a spacious retort, containing 1 part of starch and 10 parts of nitric acid of 1.3, through a mixture of 2 parts of alcohol of 85 per cent and 1 part of water, contained in a bottle of two tubulures, and surrounded by cold water. The nitrous acid is immediately absorbed by the alcohol, and combines with ether. The product, at the same time, distils over, and may be conducted from the vessel in which the reaction takes place, by means of a glass tube, to a tube condenser.

Nitrous ether, in a state of purity, is a volatile liquid, of a pale yellow colour, possessing the agreeable odour of the Normandy rennet. Its density at 59° (15° cent.) is 0.947; it boils at 61.5° (16.4° cent.). It is converted by the tincture of hydrate of potash into nitrate of potash and alcohol.

Carbonate of oxide of ethyl, carbonic ether, EO, CO_2 ; obtained by M. Ettling, by the action of potassium or sodium on oxalic ether; a colourless aromatic liquid, of density 0.965 at 66.2° (19° cent.), boiling at 258.8° (126° cent.).

Carbonate of oxide of ethyl and potash, $\text{KO}, \text{EO} + \text{C}_2\text{O}_4$; is prepared by dissolving in alcohol hydrate of potash, fused and still red hot, and saturating the solution with dry carbonic acid gas. When purified, it crystallizes in silky laminae, soft to the touch (Dumas and Peligot).

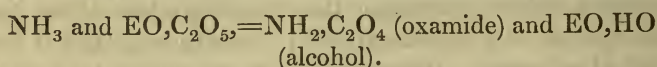
Oxalate of ether, oxalic ether, $\text{EO}, \text{C}_2\text{O}_5$. The following process is given by M. Liebig, from Ettling, for the preparation of this which is one of the most interesting of the ethers. A mixture is distilled rapidly of 4 parts of binoxalate or quadroxalate of potash, 5 parts of oil of vitriol, and 4 parts of alcohol of 90 per cent (0.818). As soon as the liquid which passes is troubled by an addition of water, it contains oxalic ether, and is collected in a receiver which is not cooled. The product is afterwards mixed with 4 times its volume of water; the ether then separates, and it is agitated immediately with pure water, which is renewed frequently, till an acid re-action ceases to be manifested.

The washed ether is rectified in a small dry retort, which is filled to 9-10ths; as soon as the product which passes is colour-

less and transparent, and the liquid boils tranquilly in the retort without bumping, it is necessary to change the receiver, for from that period the oxalic ether distils over, pure and anhydrous. The residue in the retort contains some traces of oxalic acid. (Traité, p. 350).

Oxalic ether is a colourless liquid, of an aromatic odour; its density 1.0929, and boiling point 363.2° (180° cent.). When pure it may be kept in contact with water for several days without decomposition, but if it contains the smallest trace of acid or alcohol, it is decomposed rapidly into oxalic acid and alcohol. The fixed alkalies act upon it in the same manner as water.

By ammonia or solution of ammonia in excess, oxalic ether is instantly decomposed, a beautiful white precipitate of *oxamide* (page 407) appearing and alcohol is reproduced:



Oxalate of ether and oxamide, or oxamethane; $\text{EO}, \text{C}_2\text{O}_5 + \text{NH}_2, \text{C}_2\text{O}_4$; or $\text{C}_8\text{H}_7\text{NO}_6$, is a substance in beautiful white crystalline leaflets, formed by adding alcohol saturated with ammoniacal gas to a solution of oxalic ether in alcohol. It is fusible about 212° , distils at 428° (220° cent.) without alteration. Four atoms of the hydrogen of this compound can be replaced by chlorine, and *chloroxamethane* formed, $\text{C}_8 \overset{\text{H}_3}{\underset{\text{Cl}_4}{\text{NO}_6}}$, which strikingly resembles oxamethane in its physical properties, and is even believed to be isomorphous with it.

Oxalate of oxide of ethyl and potash, oxalovinate of potash, $\text{KO}, \text{EO} + \text{C}_4\text{O}_{10}$. This salt is prepared by adding to a solution of 1 volume of oxalic ether in 2 volumes of alcohol, somewhat less than half the potash dissolved in alcohol, which would be required to form a neutral salt with the oxalic acid of the ether; the salt precipitates, being insoluble in the alcohol. It is anhydrous.

Acid oxalate of oxide of ethyl and potash, oxalovinic acid, $\text{HO}, \text{EO} + \text{C}_4\text{O}_{10}$, is obtained by treating an alcoholic solution of the preceding salt with hydrofluosilicic acid, or by decomposing with caution an aqueous solution of the oxalate of ethyl and barytes by dilute sulphuric acid. It is a very acid liquid, which is decomposed by evaporation.

Sulphocarbonate of oxide of ethyl and potash, xanthate of potash

of Zeise; $\text{KO,EO} + \text{C}_2\text{S}_4$. This salt contains 2 atoms of bisulphuret of carbon, united with 1 of potash and 1 of oxide of ethyl. It is formed on pouring the bisulphuret of carbon into absolute alcohol saturated cold with hydrate of potash, and keeping the mixture at a gentle heat; the liquor becomes a crystalline mass of the salt at 32° . The salt crystallizes in colourless or yellowish crystals.

Sulphocarbonate of oxide of ethyl and water or xanthic acid, $\text{HO,EO} + \text{C}_2\text{S}_4$, is obtained as an oily liquid, insoluble in water, when the preceding potash salt is decomposed by dilute sulphuric or hydrochloric acid.

Bicyannurate of oxide of ethyl, cyanic ether, $3\text{EO} + 2\text{Cy}_3\text{O}_3 + 6\text{HO}$. This compound was obtained by Liebig and Wœhler by directing the vapours of hydrated cyanic acid into a mixture of alcohol and ether, as long as they were absorbed. The compound crystallizes after twenty-four hours' repose, and is purified from cyamelide, with which it is accompanied, by solution in boiling alcohol or water and a second crystallization. Its solution is neutral to test paper, and it does not form compounds with metallic oxides.

Benzoate of oxide ethyl, benzoic ether, $\text{C}_4\text{H}_5\text{O} + \text{C}_{14}\text{H}_5\text{O}_3 = \text{EO,BzO}$. This is a liquid ether, of density 1.0539 at 50° (10° cent.), boiling at 408.2° (210° cent.), prepared by distilling a mixture of 4 parts of alcohol of 83 per cent. (0.840) with 2 parts of crystallized benzoic acid, and 1 part of concentrated hydrochloric acid.

Hippurate of oxide of ethyl, hippuric ether, $\text{C}_4\text{H}_5\text{O} + \text{C}_{18}\text{H}_8\text{N}_5\text{O}_5$. This compound was first prepared by Dr. Stenhouse. It is obtained in fine crystalline needles, perfectly white, and of a silky lustre. The crystals are not volatile, their density is 1.043 at 73.4° (23° cent.); they fuse at 109.4° (43° cent.)

Chloroxi-carbonic ether, $\text{C}_4\text{H}_5\text{O} + \text{C}_2\text{O}_3\text{Cl}$. This name has been given by M. Dumas to an ethereal liquid, which is formed when absolute alcohol is brought into contact with chloro-carbonic acid gas (page 378). Its density is 1.33 at 59° ; it boils at 201.2° (94° cent.).

Urethane, $\text{C}_6\text{H}_7\text{O}_4\text{N}$. This substance is formed, with sal ammoniac, on dissolving the preceding compound in solution of ammonia. Purified by distillation, it is a pearly-white, crystalline substance, resembling spermaceti; it fuses at 212° , and

distils without change at 356° (180° cent.). Urethane may be considered as a chloroxycarbonic ether, in which the chlorine is replaced by amidogen, $C_4H_5O + C_2O_3(NH_2)$. It may also be looked upon as the product of the combination of 2 atoms of carbonic ether with 1 atom of urea, $2C_5H_5O_3 + C_2O_2, N_2H_4$, the consideration which induced M. Dumas to give it the name of urethane.

Some other compound ethers or neutral salts of oxide of ethyl will be described under their respective acids.

TRANSFORMATIONS OF THE BODIES CONTAINING ETHYL.

The compound of alcohol and chloride of zinc was found by M. Masson to give ether and water when heated to 284° , and at a higher temperature, between 320° and 392° , two *liquid hydrocarbons*; one boiling at 212° represented by C_8H_7 , and the other boiling at 572° (300° cent.) C_8H_9 ; the sum of which is $C_{16}H_{16}$, exactly the composition of olefiant gas. The liquid long known as *oil of wine* is probably one of these hydrocarbons. It is found in the retort from which a considerable quantity of crude ether has been distilled off lime.

Sulphate of oxide of ethyl and of etherole, $C_4H_5O, C_4H_4 + S_2O_6$, long known as the *sweet oil of wine* or the *heavy oil of wine*. This compound arises from the decomposition of the neutral sulphate of oxide of ethyl, which cannot exist in an isolated state, and is best obtained by distilling 3 atoms of the sulphovinate of lime with 1 atom of caustic lime; these give 1 atom of sulphate of oxide of ethyl and etherole, 1 atom of alcohol, and 4 atoms of sulphate of lime. The sulphate of oxide of ethyl and of etherole is a colourless oily and aromatic liquid, of density 1.33, boiling at 536° (280° cent.), and capable of being distilled without alteration, if free from water. It is decomposed by water and by acids into sulphovinic acid and etherole. *Etherole*, first observed by Mr. Hennel, and sometimes called the *light oil of wine*, is an oily liquid, of density 0.917, boiling at 536° . Etherole submitted to a low temperature, deposits crystals of *etherine*, which are long prisms of great lustre, fusing at 230° and boiling at 500° (260° cent.); of density 0.980. These two compounds are isomeric, and consist of carbon and hydrogen, in the same proportions as in olefiant gas.

Ethionic and isethionic acids, produced by M. Magnus, by

the action of anhydrous sulphuric acid on absolute alcohol. A crystalline compound of olefiant gas and anhydrous sulphuric was obtained by M. Regnault, which may be separated by $C_4H_4 + 4SO_3$, or by $C_4H_4O, S_2O_5 + 2SO_3$, that is, as containing hyposulphuric acid united with another base, different from oxide of ethyl, with sulphuric acid. A crystalline compound was also obtained by Magnus, by exposing absolute alcohol to the vapour of anhydrous sulphuric acid, and named by him *carbyle*, which appears to be the same. Saturated with carbonate of barytes, carbyle gave free sulphuric acid and the soluble *ethionate of barytes*, which last contains the same elements as sulphovinate of barytes, indicating the assumption of the elements of an atom of water by the carbyle. *Ethionic acid* may be procured by adding dilute sulphuric acid cautiously to a solution of ethionate of barytes. It is a compound of small stability, and is decomposed by boiling like sulphovinic acid, giving alcohol and *isethionic acid*, the last of which does not undergo farther decomposition. The salts of the latter are likewise isomeric, when dried, with the sulphovinates. Isethionic acid may be concentrated, and stands 302° (150° cent.) without decomposition. All its salts are neutral to test-paper, and are also remarkably stable, supporting a temperature of 482° (250° cent.) without decomposition. When fused with an alkaline hydrate, they leave as a residue a mixture of the sulphite and sulphate of the alkali, from which it is inferred that they contain hyposulphuric acid, and not sulphuric acid.

Isethionate of barytes is prepared by passing pure olefiant gas through anhydrous sulphuric acid, in the liquid state; or by saturating ether in a flask surrounded with ice, by the same acid. The acid solution is afterwards boiled, so long as alcohol is disengaged, and then saturated with carbonate of barytes. This salt is represented by $BaO, C_4H_5O_2 + S_2O_5$. *Isethionate of copper* crystallizes in regular octohedrons, of an emerald green colour, containing 2 atoms of water of crystallization, which they lose at 482° (250° cent.), and become white and opaque. From none of these salts can alcohol or ether be derived; they do not, therefore, contain ethyl.

Two other acids of this class have been obtained, *methionic acid*, by saturating ether with anhydrous sulphuric acid, without cooling the mixture, of which the salt of barytes, $BaO, C_2H_3S_2O_7$,

is insoluble in alcohol; and *althionic acid*, which is found in the residue of the preparation of olefiant gas by means of alcohol and sulphuric acid, of which the salts are isomeric with the sulphovates, although distinguishable from them by their properties (Ettling, Regnault).

The compounds which follow are derived from the oxidation of alcohol and its derivatives.

SECTION III.

ACETYL SERIES OF COMPOUNDS.

Acetyl $C_4H_3=Ac$: a hypothetical radical, produced by the abstraction of 2 atoms of oxygen from ethyl, by oxidating processes, and which pervades a series of compounds, including acetic acid, from which it derives its name.

The following are the oxygen compounds of acetyl.

Acetyl	C_4H_3	
Oxide of acetyl	C_4H_3O	unknown
Hydrate of oxide of acetyl	$C_4H_3O + HO$	aldehyde
Acetous acid	$C_4H_3O_2 + HO$	aldehydic acid
Acetic acid	$C_4H_3O_3 + HO$	acetic acid.

HYDRATE OF THE OXIDE OF ACETYL, OR ALDEHYDE.*

Formula, $C_4H_3O + HO$. It will be observed that aldehyde occupies the same place in the acetyl series that alcohol does in the ethyl series. It was obtained in an impure state by Dobereiner, and afterwards isolated, and its true nature ascertained by Liebig. Aldehyde is formed by the action of oxidating bodies upon alcohol, by which 2 atoms of hydrogen are abstracted, and the elements of aldehyde left. It is occasionally produced during the absorption by alcohol of oxygen from the air, in the process of acetification, and is a product of the action of dilute nitric acid upon alcohol, but it is usually prepared by the action of dilute sulphuric acid with peroxide of manganese upon alcohol.

* From alcohol dehydrogenatum.

To prepare aldehyde, a mixture is distilled by a gentle heat of 6 parts of sulphuric acid, 4 parts of water, and 4 parts of rectified spirits of wine, and the product carefully condensed, so long as chemical action appears to take place from the frothing up of the materials in the retort. The distilled liquid, which is a mixture of aldehyde with water and several other secondary products, is distilled by a water-bath from an equal weight of chloride of calcium, till one half of it passes over. But to free the aldehyde from foreign bodies, it is necessary to unite it with ammonia; the product of the last distillation is therefore diluted with an equal volume of ether, and the mixture saturated at a low temperature with ammoniacal gas; the compound, or ammonia-aldehyde is deposited in colourless crystals, which are afterwards washed with ether and dried in air. Two parts of ammonia-aldehyde dissolved in 2 parts of water are distilled with 3 parts of sulphuric acid diluted with 4 parts of water, and the product condensed in a receiver surrounded with ice. It is afterwards rectified from chloride of calcium, by a heat not exceeding 77 or 86° (25 or 30° cent.).

Aldehyde is a colourless, highly-fluid liquid, of a peculiar ethereal and suffocating odour, boiling at 71.6° (22° cent.) of density 0.790 at 64.4° (18° cent.), neutral, and very combustible. It is miscible with water, alcohol and ether. It changes in the air into acetic acid by absorption of oxygen. It dissolves phosphorus, sulphur and iodine.

When pure and anhydrous aldehyde is kept for some time at 32° , it gradually loses its power to mix with water, and is transformed into a coherent mass, composed of long transparent needles, resembling icy spiculæ. This is *Elaldehyde*, which is similar in composition to aldehyde, but of three times the atomic weight, judging from the density of its vapour. *Elaldehyde* fuses at 35.6° (2° cent.), and boils at 201.2° (94° cent.).

Metaldehyde is another product of the condensation of the elements of aldehyde, which appears at the ordinary temperature in aldehyde left for some time in a well-stopped phial, in the form of white and transparent needles, or colourless prisms, which gradually attain a certain magnitude. It sublimes at 248° without fusing, and condenses in the air in snowy and very light flocks. It is insoluble in water, but dissolves easily in alcohol. The density of its vapour has not been determined.

Aldehyde is capable of combining directly with ammonia and potash, thus evincing an approach to the acid character.

Ammonia-aldehyde, $C_4H_3O, NH_3 + HO$, crystallizes in acute rhombohedrons, which are transparent, and of great lustre. These crystals fuse between 70 and 80° cent. and distil without alteration at 100° cent.

Acetal, or compound of aldehyde with ether, $AcO, EO + HO = C_8H_9O_3$, was discovered by Dobereiner, and is formed by the action of platinum black on the vapour of alcohol with the presence of oxygen. Acetal is a colourless very fluid liquid, having a peculiar odour, suggesting that of Hungary wines. It boils at 95.2° cent., its density is 0.823 at 20° cent. It is soluble in 6 or 7 parts of water, and mixes with alcohol in all proportions.

Resin of aldehyde is a product of the decomposition of aldehyde by alkalies, with the assistance of air.

ACETOUS OR ALDEHYDIC ACID.

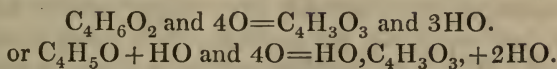
Formula of the hydrated acid, $C_4H_3O_2 + HO = AcO_2 + HO$. This acid is formed when aldehyde is heated in contact with oxide of silver, one half of the oxide being reduced to the metallic state, while the other half unites with the aldehydic acid formed. If to water in a test-tube containing a few drops of aldehyde, a little nitrate of silver be added, and ammonia so as to precipitate the oxide of silver, and then the tube be rapidly heated by the flame of a spirit-lamp, the silver is deposited on the tube with a bright surface, like a mirror, and forms a beautiful experiment. When the salts of this acid are evaporated, they become brown, and undergo decomposition.

ACETIC ACID.

Formula of the hydrated acid $HO + C_4H_3O_3 = HO + AcO_3$.

Vinegar has long been derived by the action of air upon alcoholic liquors, such as wine and beer, but the remarkable discovery of Dr. J. Davy, that platinum black in contact with alcohol became incandescent, and gave rise to acetic acid, first led Dobereiner to the discovery that alcohol by absorbing oxygen, gives rise to water and acetic acid, without disengaging carbonic acid. He found that the elements of 1 atom of alcohol absorb 4 atoms

of oxygen, with the formation of 1 atom of anhydrous acetic acid, and 3 atoms of water :



Hence, when alcohol is converted into acetic acid, 2 atoms of oxygen are directly absorbed, and 2 atoms of oxygen convert 2 atoms of hydrogen into water. The atom of water of the alcohol and the 2 atoms of water produced, are all retained, and form a remarkable terhydrate of acetic acid.

Pure alcohol, diluted with water and exposed to air, does not acidify; the presence of some foreign organic matters, which exist in wine and beer, is necessary to act as a ferment, and to place the alcohol in a condition to absorb oxygen. This ferment is no doubt an oxidable azotised matter. Some kinds of beer, in which the ferment has been completely exhausted and precipitated by a preceding highly-protracted vinous fermentation, such as the Bavarian beer, are not liable to become sour or undergo the acetous fermentation. The rapid process of acidifying alcohol, introduced into Germany by MM. Wageman and Schutzenbach, is the most interesting, in a scientific point of view.

Strong alcohol is diluted with 4 or 6 parts of water, and about 1-1000th of yeast, must of beer, vinegar or honey added to it. To acidify this liquid, it is heated to 75 or 80°, and made to trickle through a cask, filled with beech-wood shavings, (Fig. 95), and pierced with holes at top and bottom to allow a circulation of air through it. From the great surface exposed by the liquid, the absorption of oxygen is most rapid, and the temperature rises to 100 or 104°. When the liquid has been passed three or four times through the barrel, at the high temperature, all the alcohol it contains is changed into vinegar; an operation which may be completed in twenty-four or thirty-six hours. The addition of certain aromatic substances, such as the essential oils, or a mere trace of wood vinegar, entirely prevents the acidification of the alcohol.

FIG. 95.



Wood vinegar, or pyroligneous acid is prepared on a large

scale by the distillation of wood, generally that of oak coppice deprived of the bark, which is used in tanning. The watery fluid containing the acid, and tarry matter which distil over together, are separated, mechanically, in a great measure, by subsidence. The acid may be freed from a portion of the empyreumatic oils it holds in solution, by a single distillation. It is purified completely by neutralising it with lime, crystallizing the acetate of lime repeatedly, decomposing the latter by sulphate of soda, and fusing the acetate of soda by a high temperature, at which the empyreumatic matters are volatilised or destroyed. By distilling 3 parts of the acetate of soda, well dried and in powder, with 9.7 parts of sulphuric acid, a highly concentrated and pure acetic acid is obtained.

The proportions last mentioned give 2 parts of a hydrated acetic acid, which is distilled again, and the two last thirds of distilled liquid exposed to 24 or 25°, for the protohydrate of acetic acid, which crystallizes. The crystals may be drained, fused, and crystallized again, to obtain the hydrate of acetic acid in a state of purity. Below 63°, the hydrate crystallizes in shining transparent plates or tables, which fuse above 63° into a limpid liquid, of density 1.063; it boils at 248°. The odour of this acid is penetrating and characteristic; it forms blisters on the skin, like a mineral acid. The liquid acid mixes with water, alcohol, ether, and several essential oils in all proportions. It dissolves camphor and some resins. The vapour of the acid in a state of ebullition may be kindled, and burns with a pale blue flame, producing water and carbonic acid. Nitric acid has no action on acetic acid; sulphuric acid with heat blackens acetic acid, with an evolution of sulphurous acid.

Acetic acid increases somewhat in density by a slight dilution; the greatest condensation occurring in the hydrate consisting of 1 atom of anhydrous acid and 3 atoms of water, of which the density is 1.07. The strength of a dilute acetic acid is best ascertained by the quantity of marble it dissolves.

Acetic acid forms neutral salts, and with many metallic oxides sub-salts containing 2 and 3 atoms of base to 1 atom of acid. Most of its neutral salts are soluble. It is recognised in combination by the peculiar odour of acetic acid evolved when concentrated sulphuric acid is added. M. Liebig recommends as the most certain means of discovering the presence of acetic acid, or of an acetate in any substance, to distil it with

dilute sulphuric acid, and to place the product in contact with oxide of lead in the cold. If there is any acetic acid present, the oxide of lead dissolves, and the solution exhibits an alkaline reaction. (Traité, i. 398).

Acetate of oxide of ethyl, acetic ether, $C_4H_5O + C_4H_3O_3 = EO, \bar{A}$. Alcohol is only decomposed to a small extent when distilled with strong acetic acid. The ether is prepared by distilling, with a heat moderate at first, but afterwards increased, 4.5 parts of strong alcohol and 6 parts of concentrated sulphuric acid, previously mixed and cooled, with 16 parts of anhydrous acetate of lead. The product is neutralised with a little lime, then poured over an equal bulk of chloride of calcium in a tubulated retort, and distilled again by a water-bath. Acetic ether is a liquid of an agreeable refreshing odour, and is the source of the refreshing odour of some kinds of vinegar which contain it. Its density is 0.89 at 59° ; it boils at 165.2° (74° centig.). Acetic ether is soluble in 7 parts of water, and in alcohol and ether in all proportions. It is decomposed by alkalies with the greatest facility.

Acetic acid forms neutral and bisalts with the alkalies. The neutral solution of *acetate of ammonia*, the spirits of mindererus, is used in medicine. *Acetate of potash* is a foliated crystalline mass, anhydrous, and slightly deliquescent. *Acetate of soda* crystallizes with 6 atoms of water; it is soluble in three times its weight of cold water, and in five times its weight of alcohol. Its taste is saline, cooling and agreeable. *Acetate of barytes* crystallizes below 59° with 3 atoms of water, and is isomorphous with acetate of lead; at a higher temperature it crystallizes with 1 atom of water. It is very soluble in water, and more so at a low than at a high temperature. *Acetate of strontian* crystallized below 59° (15° cent.) contains 4 atoms of water, and crystallized above that temperature only half an equivalent of water. *Acetate of lime* crystallizes with water. A concentrated and boiling solution of it treated with sulphate of soda, in the preparation of acetate of soda, allows a double *sulphate of lime and soda* to precipitate. *Acetate of magnesia* is very soluble, and crystallizes with difficulty.

Acetate of alumina is obtained in solution, when acetate of lead barytes or lime is precipitated by sulphate of alumina, and is

much used in dyeing. This salt is decomposed in drying, or by a slight heat, into free acetic acid and a subacetate of alumina which is insoluble. The solution of the pure salt may be boiled without decomposition, but if sulphate of potash, or any other neutral salt of an alkali be present, the solution becomes turbid when heated, and a basic salt precipitates, which dissolves again on cooling (Gay-Lussac). *Acetate of manganese* is used in dyeing, and is prepared for that purpose by mixing acetate of lime with sulphate of manganese. This salt is crystallizable. *Acetate of zinc* crystallizes with 3 atoms of water. *Acetates of iron*: a mixture of the acetates of protoxide and peroxide of iron, employed as a mordant for dyeing black, is prepared directly by dissolving old iron hoops, &c. in crude wood vinegar, with access of air. The *acetates of lead* have already been described (page 594); also the *acetates of copper* (page 584), acetate of black oxide of mercury (page 653), and acetate of silver (page 673).

SECTION IV.

PRODUCTS OF THE ACTION OF CHLORINE, BROMINE, AND IODINE UPON ETHYL, ACETYL, AND THEIR COMPOUNDS.

Oxichloride of ethyl, $C_4H_3Cl_2O$, (1), is an oily colourless liquid, obtained by saturating anhydrous ether with dry gaseous chlorine, cooling the mixture at the beginning, and heating it towards the end of the operation. As in the formation of acetic acid, 2 atoms of hydrogen are oxidated and withdrawn by the action of the oxygen of the air upon alcohol, and replaced by 2 atoms of oxygen, so in the action of chlorine upon alcohol, a similar change occurs, of which the product is the oxichloride of acetyl. When heated with potassium, this compound gives chloride of potassium, and a gaseous body, containing only half the chlorine in the original substance, or C_4H_3ClO , (2), observed by Malaguti. By the action of chlorine upon the vapour of pure ether in sun-shine Regnault obtained another crystalline compound C_4Cl_5O , (3), in which the whole hydrogen of ether is replaced by chlorine. Felix d'Arcet has also observed an accessory product in the

preparation of Dutch liquid, which had the composition C_4H_4ClO , (4). It is named *chlorethèral* by him. It will be observed that the fourth, first and third of these bodies are compounds, in which 1, 2 and 5 atoms of the hydrogen of chloride of ethyl are replaced by chlorine, without any other change of composition. They are all neutral bodies.

Oxisulphuret of acetyl, $C_4H_3S_2O$; a compound in which 2 atoms of the hydrogen of oxide of ethyl are replaced by 2 atoms of sulphur, is obtained by the action of sulphuretted hydrogen upon the oxichloride of acetyl. Another compound is formed at the same time, in which 1 atom of chlorine remains, and only 1 atom of sulphur is introduced, C_4H_3ClSO .

Acetate of oxichloride of acetyl, $C_4H_3Cl_2O + \bar{A}$, a body formed by the action of chlorine upon acetic ether, in which 2 atoms of the hydrogen of the ether are replaced by 2 atoms of chlorine; or the oxichloride of acetyl is formed, and continues in combination with the acetic acid. The benzoate of oxide of ethyl gives a compound, of which the formula is $BzCl + C_4H_3Cl_2O$.

Chloroxalic ether, $C_6Cl_5O_4$ or $C_4Cl_5O + C_2O_3$; formed by the action of chlorine on oxalic ether, crystallizable, fusible at 291° , not volatile. *Chloroxamethane*, $C_6Cl_5O_4 + C_2O_2.NH_2$; formed by the action of ammoniacal gas on the ether, crystallizable, fuses at 273° , boils above 392° , volatile. *Chloroxalovinic acid* is obtained by the action of solution of ammonia upon chloroxamethane (Malaguti, An. de Chim. lxxiv, 299).

Chloride of acetyl, &c.—The following table exhibits the composition and some of the properties of the series of compounds formed by Regnault, by treating the chloride of ethyl and the products thus obtained, successively with chlorine (An. de Ch. lxxi, 353):

	Spec. grav.	Boiling point.	Density of vapour.	
$C_4H_5Cl_1$	0.874*	11° centig.	2219	4 vol.
$C_4H_4Cl_2$	1.174	64° ..	3478	..
$C_4H_3Cl_3$	1.372	75° ..	4530	..
$C_4H_2Cl_4$	1.530	102° ..	5799	..
$C_4H_1Cl_5$	1.644	146° ..	6975	..

* At 11° cent.; the others between 18 and 20° cent.

CHLORAL.

Formula : $C_4HCl_3O_2 = C_4Cl_3O + HO$.

This singular liquid, of which we owe the discovery to Liebig, may be considered as the hydrate of oxide of acetyl (aldehyde), in which the whole hydrogen of the acetyl is replaced by chlorine :

Hydrate of oxide of acetyl . . . $C_4H_3O + HO$.

Chloral $C_4Cl_3O + HO$.

It cannot, however, be prepared directly by the action of chlorine upon aldehyde, owing to the facility with which the latter body changes, but it is the ultimate product of the action of chlorine upon anhydrous alcohol. It is recommended in preparing chloral, to introduce a few ounces of perfectly anhydrous alcohol into the body of a tubulated retort, supported with its beak somewhat elevated, and with a glass tube adapted by a cork to the mouth, and directed upwards, so that what condenses may flow back into the body of the retort. Chlorine gas carefully dried by being passed through sulphuric acid, which is renewed from time to time during the process, is conducted by a tube entering the tubulure of the retort, and made to stream through the alcohol, the body of the retort being immersed in cold water to keep it cool at the beginning, but afterwards heated to assist in expelling the hydrochloric acid formed, towards the end of the process. An immense quantity of chlorine is required, and the gas may continue to be absorbed by a few ounces of alcohol for twelve or fifteen hours. The operation is complete when the chlorine traverses the boiling liquid without any disengagement of hydrochloric acid; a dense oleaginous liquid, the hydrate of chloral, is obtained, which often becomes a solid mass on cooling. The mass is fused by a gentle heat, and mixed in a well-stopt bottle, with two or three times its bulk of oil of vitriol, and the mixture gently heated by a water-bath; the impure chloral comes to the surface of the liquid, in the form of a limpid oil. It is drawn off, and boiled for some time to expel free hydrochloric acid and alcohol, and then distilled from an equal bulk of sulphuric acid, to deprive it of adhering water. The last product is pure chloral, except a little hydrochloric acid, which is separated by distilling again

from quicklime slaked and recently ignited, discontinuing the distillation when the lime in the retort is no longer covered by the liquid; the product obtained is chloral, perfectly pure. (Liebig).

Chloral is a pretty fluid oleaginous liquid, colourless, greasy to the touch, having a penetrating disagreeable odour which provokes tears; its taste is first oily and then caustic. Its density is 1.502 at 64.4° (18° cent.), and it boils at 201.2° (94° cent.) distilling without alteration; the density of its vapour is very nearly 5000, and its combining measure, 4 volumes (Dumas). Chloral is miscible with alcohol and ether; it dissolves, apparently without alteration, sulphur, phosphorus and iodine, with the aid of heat.

Hydrate of chloral.—Chloral is first obtained from alcohol in the state of a hydrate, the water being derived from a reaction of the nascent hydrochloric acid and alcohol, which gives rise to water and chloride of ethyl. When pure chloral is brought in contact with a small quantity of water, combination takes place immediately on mixing the liquids, with evolution of heat, and in a few seconds the compound is deposited as a crystalline mass, composed of needles, which re-dissolve in a larger quantity of water. By evaporation of the solution in vacuo, the compound is obtained in large rhombohedral crystals, which contain 2 atoms of water. The solution of the hydrate of chloral is neutral, and has no action on red oxide of mercury; the dry hydrate may be distilled without change.

Insoluble chloral.—Like aldehyde pure chloral cannot be kept long without alteration. It gradually passes into a solid mass resembling porcelain, without change of weight, and equally whether contained in vessels which are hermetically sealed or open. This mass is not dissolved by water, but when placed in contact with a very small quantity of water, it slowly changes into the crystalline hydrated chloral, which dissolves at once when a large quantity of water is added to it. Insoluble chloral is modified by contact with sulphuric acid, and somewhat altered in composition; when washed with water it loses a little hydrochloric acid, and acquires some water. The formula assigned to *modified insoluble chloral* is $C_{12}H_4Cl_8O_7$: which is 3 atoms of chloral, minus 1 atom of hydrochloric acid plus 2 atoms of water.

Sulphuret of ether with chlorine.—Regnault has observed that the sulphuret of ethyl is powerfully acted upon by chlorine, with the assistance of light; 4 atoms of hydrogen are replaced by 4 atoms of chlorine, and the compound $C_4 Cl_4 HS$ formed, which is a fetid liquid, boiling about 320° (160° cent.); of density 1.673 at 75.2° (24° cent.)

Chloracetic acid, $C_4 Cl_3 O_3 + HO$.—This remarkable acid, in which the 3 atoms of the hydrogen of acetic acid are replaced by 3 atoms of chlorine, was obtained, by M. Dumas, by the action of chlorine gas contained in large balloons upon the hydrate of acetic acid, exposed to the direct rays of the sun for a whole day. It crystallizes in rhomboidal plates or colourless needles, which deliquesce rapidly in damp air. Chloracetic acid whitens the tongue; its vapour is suffocating and painful to the organs of respiration. It reddens litmus, without bleaching it. The crystals fuse at 45 or 46° cent.; and fused they enter into ebullition between 195 and 200° cent. The density of the fused acid at 46° cent. is 1.617. It forms a class of salts which greatly resemble the acetates; they are all soluble, and are blackened by an excess of alkali even more readily than the acetates.

Chloracetic acid exhibits a beautiful transformation when heated in contact with an alkali; it is decomposed into perchloride of formyle, a metallic chloride, and alkaline carbonate and formiate. Acetic acid gives in the same circumstances light carburetted hydrogen ($C_2 H_4$) and an alkaline carbonate. (Dumas, An. de Ch. lxxiii, 77 and 89).

Heavy chlorinated ether.—The body which principally is formed when alcohol of 80 per cent. (0.848) is saturated with humid chlorine gas. It precipitates from the acid liquid when water is added. It is colourless, neutral, of density 1.277, and boils between 112 and 125° cent. The results of its analysis are discordant, which M. Regnault supposes to arise from intermediate chlorinated bodies, which form between aldehyde and chloral:

Aldehyde.	.	.	$C_4 H_4$	O_2
Intermediate bods.			$C_4 H_3 Cl$	O_2
			$C_4 H_2 Cl_2$	O_2
Chloral.	.	.	$C_4 H Cl_3$	O_2

Bromal, $C_4 Br_3 O + HO$.—This compound, which corresponds with chloral, was formed by M. Lœwig by adding 13.8 parts of bromine to 1 part of alcohol cooled by ice, adding the former in small portions, taking care that the part previously added had first disappeared. It is purified in the same manner as chloral. Bromal is a colourless oily liquid of a peculiar and very strong odour which provokes tears, and of a caustic taste. Its density is 3.34, and boiling point below 212° . Bromal is miscible with water, alcohol and ether. Caustic alkalis transform it into an alkaline formiate and perbromide of formyl. Its solution affords by evaporation a crystalline hydrate, containing 4 atoms of water, consequently 2 atoms more than the hydrate of chloral.

Brominated ether.—Lœwig has observed, that bromine in acting upon ether, produces a body analogous to heavy chlorinated ether, but respecting the composition of which there is the same uncertainty.

Iodal.—An oleaginous liquid which corresponded in some properties with chloral, was obtained by M. Aimé, by the action of 4 parts of alcohol, one part of iodine, and one part of fuming nitric acid, left in contact in a bottle imperfectly closed; but its composition was not ascertained. Mr. Johnston had previously obtained some peculiar substances by a similar reaction.

Chloride of cyanogen upon alcohol.—A slightly volatile crystalline matter is produced, when a mixture of alcohol and very concentrated hydrocyanic acid, or a mixture of alcohol and a metallic cyanide soluble in alcohol, is saturated with dry chlorine. This crystalline substance has a silky lustre, and considerably resembles sulphate of quinine. It fuses at 248° , subliming in part. Its empirical formula is $C_{16} H_{14} O_8 Cl_2 N_2$, corresponding with 3 atoms of aldehyde $3(C_4 H_4 O_2)$, 2 atoms of chlorine Cl_2 , 2 atoms of cyanogen $N_2 C_4$, and 2 atoms of water $H_2 O_2$. (Stenhouse).

SECTION V.

CONGENERS OF ALCOHOL OF AN UNCERTAIN CONSTITUTION.

Hydruret of acetyl, olefiant gas, etherine, elayl (Berzelius); $C_4 H_4 = C_4 H_3, H$ or AcH .—This gas is generally prepared by

heating a mixture of 1 part of alcohol with 6 or 7 parts of concentrated sulphuric acid (page 426); and is accompanied by sulphurous acid, the vapour of ether, the double sulphate of oxide of ethyl and etherole (page 772), from all of which it is purified by passing it first through milk of lime, and then through oil of vitriol. M. Mitscherlich finds it to be formed almost exclusively, when alcohol is brought into contact with oil of vitriol heated to 320° (page 772).

Pure hydruret of acetyl has a feeble ethereal odour; it is only very slightly soluble in water, oil of vitriol, alcohol and ether. It forms a crystalline compound with anhydrous sulphuric acid, $C_4 H_4 + 4SO_3$. It combines with chlorine gas in equal volumes, and forms an oily liquid (a property from which it received the name of olefant gas), the chlorhydrate (hydrochlorate) of the chloride of acetyl, known as Dutch-liquid, or the oil of olefant gas.

Chlorhydrate of chloride of acetyl, $C_4 H_3 Cl$, $H Cl$, or $Ac Cl$, $H Cl$.—Is purified by mixing with water and distilling the product last mentioned, by a water bath; depriving it afterwards of the water which it takes up by shaking it in a bottle with sulphuric acid, and distilling again by a water bath. It is a very fluid colourless liquid, of an agreeable ethereal odour and sweetish taste; boils at 82.4° cent.; density of its vapour 3448.4. It communicates its odour to water without dissolving sensibly in it, but is soluble in all proportions in alcohol and ether. This compound may be distilled from hydrate of potash without change, but is gradually decomposed by an alcoholic solution of potash into chloride of potassium and chloride of acetyl; when this compound is heated with potassium, hydrogen gas and the chloride of acetyl are disengaged.

Chlorhydrate of chloride of acetyl readily absorbs chlorine, and by the continued action of that body a product is obtained, which by distillation furnishes two new compounds, one at 235° (115° cent.) $C_4 H_2 Cl_2$, $H Cl$; and another at 275° (135° cent.) $C_4 H_2 Cl_4$. The last compound by the continued action of chlorine in diffuse day-light, or more rapidly when exposed to the direct rays of the sun, is converted into the crystalline prochloride of carbon, $C_4 Cl_6$ (page 377).

Chloride of acetyl, $C_4 H_3 Cl$, $= Ac Cl$, separates from the alcoholic solution above referred to, in the form of gas, by the

effect of a gentle heat; the gas is purified from adhering vapours of alcohol and water, by passing it through sulphuric acid. This gas has an odour which suggests that of garlic; its density is 2166, and combining measure 4 volumes. It is condensed into a limpid liquid at -0.6° (-17° cent.)

Chloride of acetyl is absorbed by perchloride of antimony (Sb Cl_5), and when the saturated solution is diluted with water, an ethereal liquid separates, consisting of a mixture of chloride of acetyl and hydrochloric acid, with a new compound $\text{C}_4\text{H}_3\text{Cl}_3$, or $\text{C}_4\text{H}_2\text{Cl}_2 + \text{H Cl}$. This last when distilled with an alcoholic solution of potash is resolved into chloride of potassium, water and another new volatile liquid, $\text{C}_4\text{H}_2\text{Cl}_2$, or $\text{C}_2\text{H Cl}$. Lastly, by continuing the action of chlorine upon the preceding bodies, the compound $\text{C}_4\text{H}_2\text{Cl}_4$ is obtained, or rather $\text{C}_4\text{H Cl}_3 + \text{H Cl}$, for potash transforms it into $\text{C}_4\text{H Cl}_3$, and chloride of potassium. (Regnault).

Bromhydrate of bromide of acetyl, $\text{C}_4\text{H}_3\text{Br} + \text{H Br}$, is a colourless liquid, boiling at 129.5° cent., obtained by passing olefiant gas into bromine.

Bromide of acetyl, $\text{C}_4\text{H}_3\text{Br} = \text{Ac Br}$, a gaseous body of density 3691, of which the preparation is the same as that of chloride of acetyl.

Iodhydrate of iodide of acetyl, $\text{C}_4\text{H}_3\text{I} + \text{H I}$.—This compound is slowly produced when iodine is left in a bottle of olefiant gas at the ordinary temperature, and sublimes in white crystals; but it is best prepared, according to Regnault, by heating iodine to 122 or 140° in a convenient vessel, and introducing pure olefiant gas into it, till all the iodine is converted into a pulverulent yellow or white substance. The compound fuses at 172.4° (78° cent.), and may be sublimed in olefiant gas, but not in air without decomposition. When heated with hydrate of potash and alcohol, there is a disengagement of olefiant gas and formation of iodide of potassium, and other products which have not been studied. This body does not furnish products corresponding with those derived from the chlorhydrate of the chloride of acetyl, when decomposed; it is very doubtful, therefore, whether the former is similar in constitution to the latter, as represented above.

Chloroplatinate of chloride of acetyl, $\text{C}_4\text{H}_3\text{PtCl}_2 = \text{C}_4\text{H}_3\text{Cl} +$

PtCl_2 , or $\text{AcCl} + \text{Pt Cl}$.—This compound is formed by the action of bichloride of platinum upon alcohol, together with aldehyde, but it is best prepared from a double compound, which it forms with chloride of potassium or chloride of ammonium. Pure bichloride of platinum containing no free nitric acid is dissolved in alcohol; a small quantity of free hydrochloric acid, and a quantity of chloride of potassium equal to one eighth of the weight of the bichloride of platinum are added to this solution, and the whole digested for several hours at the temperature of boiling water. The excess of alcohol is removed by distillation, and the residue saturated with carbonate of potash. By evaporating at a gentle heat the compound in question is obtained in the crystalline form, and may be purified by new crystallizations. (Liebig's *Traité*). By dissolving this compound in a little water and adding bichloride platinum to the solution, so long as the double chloride of platinum and potassium precipitates, a yellow liquid is obtained, which ought to be evaporated in a dry vacuum in the absence of light. There results a gummy mass of a honey yellow colour, liable to be blackened by light, which is the chloroplatinate of the chloride of acetyl. It dissolves slowly in water and alcohol; these solutions have an acid reaction. The hydrochloric acid of Dutch-liquid being represented by proto-chloride of platinum, Pt Cl , the compound described and Dutch-liquid may be considered as analogous:

Chlorhydrate of chloride of acetyl. . . $\text{Ac Cl} + \text{H Cl}$.

Chloroplatinate of chloride of acetyl. . . $\text{Ac Cl} + \text{Pt Cl}$.

But various other views of the constitution of this compound have been proposed.

Chloroplatinate of chloride of acetyl and potassium, Ac Cl , $\text{Pt Cl} + \text{K Cl}$.—The discovery of this salt, of which the preparation has just been described, is due to Berzelius. It crystallizes in semi-transparent regular prisms, of a lemon yellow colour, which abandon 4.625 per cent of water of crystallization at 212° and become quite opaque. It is soluble in alcohol, and also in 5 parts of hot water, and is less soluble in cold water. The solution is partially decomposed when heated to 194° , metallic platinum being precipitated and hydrochloric acid

liberated, which last protects the salt from further decomposition.

Chloride of ammonium and chloride of sodium form corresponding double salts with the chloroplatinate of chloride of ethyl.

Ammoniacal chloroplatinate of chloride of acetyl.—Ammonia or the carbonate of ammonia throws down a lemon yellow precipitate from the solution of these double compounds, in which the chloroplatinate of chloride of acetyl is united with the elements of one atom of ammonia: $\text{Ac Pt Cl}_2 + \text{NH}_3$. It is soluble in alcohol; sparingly soluble in cold water; and its solution cannot be evaporated without decomposition.

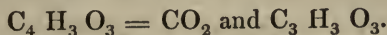
SECTION VI.

PRODUCTS OF THE ACTION OF HEAT UPON THE ACETIC ACID OF THE ACETATES.

ACETONE.

Syn. *Pyroacetic spirit, mesitic alcohol, bihydrate of mesitylene* (Kane). Empirical formula $\text{C}_3 \text{H}_3 \text{O}$.

The vapour of strong acetic acid passed through a porcelain tube heated to dull redness is decomposed without the deposition of any charcoal, being converted entirely into the vapour of acetone, which condenses, and a mixture of gases, containing carbonic oxide, carbonic acid and carburetted hydrogen. If the temperature exceeds a dull red heat, the products are a brown empyreumatic oil, inflammable gases and a deposit of charcoal. Anhydrous acetic acid contains the elements of 1 atom of carbonic acid and 1 atom of acetone :



The acetates of the stronger bases which retain carbonic acid at a red heat, when submitted to destructive distillation become carbonates, and supply no volatile product except acetone. The acetates of earths of which the carbonates are decomposed at a red heat, such as magnesia, afford a mixture of acetone

and carbonic acid, when distilled; and acetates of bases which are easily reduced, such as the acetates of copper and silver, yield hydrated acetic acid, carbonic oxide, carbonic acid, water and acetone, the residuum containing a mixture of the metal and highly divided charcoal. Acetone also appears among the products of the distillation with an alkali of sugar and other ternary compounds of carbon, oxygen and hydrogen (page 710).

Acetone may be conveniently prepared by distilling a mixture of 2 parts of crystallized acetate of lead and 1 part of quicklime in a salt-glaze jar (greybeard), the lower part of the jar being coated with fire-clay, and a bent glass tube half an inch in diameter adapted to the mouth by a cork, so as to form a distillatory apparatus. The jar is supported in the mouth of a small furnace, by which the lower part of the jar only is heated to redness, and the vapours conducted into a Liebig's condenser. The product is redistilled from quick lime repeatedly, till its boiling point is constant at 132° .

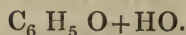
Acetone is a limpid colourless liquid, having a peculiar penetrating and slightly empyreumatic odour. Its density in the liquid state is almost the same as that of alcohol 0.7921, and the density of its vapour 2022, air being 1000; its taste is disagreeable and analogous to that of peppermint. It is miscible in all proportions with water, alcohol and ether. Many salts which are soluble in alcohol and water are insoluble in acetone, particularly chloride of calcium and hydrate of potash; acetone is separated from water, by dissolving such salts in the mixture of these liquids. Acetone is highly inflammable and burns with a white flame.

On rectifying acetone derived from the acetates, a less volatile oleaginous body remains in the retort, which has been examined by Dr. Kane and named *dumasine*. This empyreumatic oil has a disagreeable odour and burning taste; it boils at 248° (120° cent.); its composition is expressed by $C_{10}H_8O$; the density of its vapour is 5204, and its combining measure 4 volumes.

Metacetone, C_6H_5O , which is also obtainable from sugar, has already been described.

Dr. Kane who examined acetone and the products of its decomposition several years ago, then assigned to the former

the constitution of an alcohol, doubling its atomic weight and giving it the formula :



The bodies derived from it, which I can only notice very shortly, were named by him on that theory.

Mesitylene, $\text{C}_6 \text{H}_4$.—This hydrocarbon is an oily colourless liquid, obtained on distilling acetone with half its volume of fuming sulphuric acid. It is obviously formed by the abstraction of the elements of 2 atoms of water from acetone. Sulphuric acid, nitric acid and chlorine react upon mesitylene in the same way as they do upon benzin (benzole). Mesitylene is lighter than water; it boils at 276.4° (135.5° cent.) Later in the distillation of the materials which yield that oil, another oil which resembles it much passes over, but of which the boiling point is more elevated. The formula of the second oil appears to be $\text{C}_6 \text{H}_3$.

Oxide of mesityle, $\text{C}_6 \text{H}_5 \text{O}$ (Kane).—Is obtained on adding caustic potash to the chloride of mesityle; a limpid colourless liquid, not miscible with water, having the odour of pepper-mint; it boils at 248° .

Chloride of mesityle, $\text{C}_6 \text{H}_5 \text{Cl}$ (Kane).—Produced by the direct action of hydrochloric acid upon acetone, or by adding 2 parts of perchloride of phosphorus gradually to 1 part of acetone. An oily liquid denser than water, and not miscible with that liquid.

Chloroplatinate of oxide of mesityle, $\text{C}_6 \text{H}_5 \text{O}$, Pt Cl_2 (Zeise); named *metacechlorplatin* by Zeise.—Obtained by distilling a solution of 1 proportion of bichloride of platinum with $2\frac{1}{2}$ proportions of acetone, when hydrochloric acid and an ethereal body pass over into the receiver, and a brown acid residue is left in the retort. The residue contains a resinous matter which Zeise names the *resin of platinum*; the aqueous solution derived from washing the resin, becomes turbid after a time, and deposits the compound in question in small yellow crystals which lose nothing at 212° . It is slightly soluble in water; the solution is decomposed by ebullition. When the mother liquor of these crystals is distilled, there is a disengagement of gas,

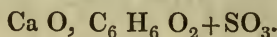
and a black flocculent powder is precipitated, which is explosive by heat. Zeise has named it *pyracechlorplatin*.

Sulphomesitic acid.—By the action of fuming sulphuric acid upon acetone there is produced among other products, an acid of which the salt of lime is expressed by :



This salt loses the elements of half an atom of water by heat. Its acid does not correspond with sulphovinic acid as the saturating power of the sulphuric acid in the former is not injured by the acetone, while it is diminished one half by the oxide of ethyl in the latter. Nor can acetone be reproduced from sulpho-mesitylic acid by any means. Acetone likewise affords no peculiar acid by its oxidation, as alcohol does acetic acid. Hence acetone is deficient in what are now considered the three most essential characters of an alcohol.

When 2 measures of acetone are mixed with 1 measure of hydrate of sulphuric acid, and the liquid diluted with water and neutralised with lime, a new salt is obtained analogous to the former, but containing twice as much acetone :



The acid of these salts undergoes decomposition when deprived of its base by sulphuric acid, and evaporated.

By the action of nitric acid upon acetone Dr. Kane obtained the two following bodies, the composition of which, however, is somewhat doubtful :

Nitrite of oxide of pteleyl. . . . $\text{C}_3 \text{H}_3 \text{O} + \text{NO}_3$;

Mesitic aldehyde. $\text{C}_3 \text{H}_3 \text{O}_2$.

By the action of phosphoric acid and of phosphorus with iodine, two acids were also obtained : *phosphomesitylic acid* and *hyphosphomesitylous acid*, the formula of the salt of barytes of the latter being, $\text{Ba O}, \text{C}_6 \text{H}_6 \text{O}_3 \text{P}$.

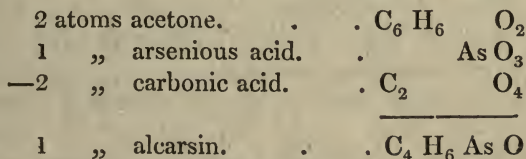
Mesitic chloral, $\text{C}_6 \text{H}_4 \text{Cl}_2 \text{O}_2$ (Dumas, Kane).—Obtained by passing dry chlorine through acetone, till the disengagement of hydrochloric acid ceases. It is a liquid of a penetrating insupportable odour, insoluble in water; density 1.33, and boiling point 258.8° (126° centig.)

Chloride of pteyleyl, $C_3 H_3 Cl$ (Kane).—A crystalline substance obtained by passing a current of chlorine into mesitylene.

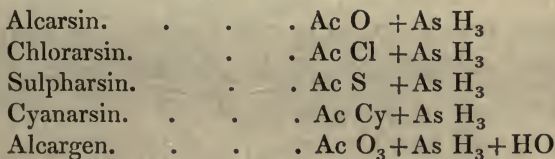
SECTION VII.

ARSENICAL COMPOUNDS DERIVED FROM ACETYL.

By the dry distillation of equal weights of acetate of potash and arsenious acid, a remarkable liquid is obtained known as the *liquor of Cadet* or *alcarsin*. This liquid may be supposed to be formed by the abstraction of 2 atoms of carbonic acid from the elements of 2 atoms of acetone and 1 atom of arsenious acid:



This is a body remarkable for its insupportable odour and spontaneous inflammability in air. The mode of formation and oxidability of alcarsin, favour the idea that it belongs to the acetyl series and contains arsenietted hydrogen. In the following scheme of the composition of alcarsin and its derivatives, the former is represented as containing the hypothetical oxide of acetyl and arsenietted hydrogen (Liebig):



Berzelius, however, considering the pre-existence of arsenietted hydrogen in these compounds as improbable, presumed alcarsin to be the oxide of a compound radical, which he named *cacodyl* (from *κακος* and *ὄδυνε*), in reference to the repulsive odour of alcarsin. The same theory is adopted by M. Bunsen, who has devoted great labour and much ingenuity to the painful investigation of this class of bodies, of which the sensible properties are most offensive and dangerous. M. Bunsen has

succeeded also in isolating cacodyl, the supposed radical of the series, a discovery of much interest for the theory of compound radicals.

CACODYL.

Formula $C_4 H_6 As = Kd$.

Cacodyl is a liquid obtained from the continued digestion of the chloride of cacodyl with metallic zinc at 230° , and dissolving out the chloride of zinc formed by water. It is dried by quicklime, distilled in a glass retort filled with carbonic acid to exclude air and crystallized repeatedly at 21.2° (-6° centig.)

Cacodyl is an ethereal limpid liquid (greatly resembling its oxide), of a nauseous odour, which crystallizes in shining prisms at 23° . It takes fire spontaneously in air and in chlorine gas, with the formation of a cloud of white smoke. It sinks in water, in which liquid it is insoluble; it is soluble in alcohol and ether. Its boiling point is about 338° (170° cent.); the density of its vapour by experiment 7101, by theory 7281; its combining measure 2 volumes. Its vapour is decomposed at a red heat into arsenic, olefiant gas and light carburetted hydrogen.

Oxide of cacodyl, alcarsin, $C_4 H_6 As + O = Kd O$.—Is prepared by the distillation of a mixture of equal weights of dry acetate of potash and arsenious acid. At the same time metallic arsenic distils over, with acetic acid and acetone which float in the receiver above the fluid alcarsin. The latter is obtained pure by washing with water free from air, and by distillation from quicklime in a retort filled with hydrogen gas, and from which atmospheric air is most carefully excluded. Oxide of cacodyl is also produced by the direct oxidation of cacodyl from slow access of air; and also from the partial reduction of cacodylic acid by phosphorous acid.

Oxide of cacodyl is an ethereal limpid liquid, of very considerable refracting power, 1.762; it boils at about 302° (150° cent.), and solidifies in the form of white silky plates at -9.4° (-23° cent.) Its odour suggests that of arseniетted hydrogen, is most disgusting, and provokes a copious flow of tears. The density of its vapour is 7555 by experiment, and 7833 by theory; its combining measure 2 volumes. It takes fire spontaneously in air and burns with a white flame and strong odour. Taken internally alcarsin is a violent poison.

Oxide of cacodyl is but slightly soluble in water, but dissolves in all proportions in alcohol and ether. It dissolves in caustic potash colouring the latter brown; dilute nitric acid dissolves it without disengagement of gas, but when heated decomposition occurs. Oxide of cacodyl dissolves phosphorus, sulphur and iodine; the solution of the last is colourless and deposits crystals, which disappear again when an excess of iodine is added. It combines with the hydrate of sulphuric acid, forming thin needles which have an acid reaction and are deliquescent. Besides combining with acids, oxide of cacodyl combines also with salts. When its solution in alcohol is mixed with a solution of chloride of mercury, a white precipitate falls, soluble in hot water and crystallizing from it, which is a compound of 1 atom oxide of cacodyl, and 2 atoms chloride of mercury. This compound is inodorous. It yields with hydrochloric acid, chloride of mercury and chloride of cacodyl. Oxide of cacodyl forms a similar compound with bromide of mercury. It reduces the salts of the suboxide and oxide of mercury.

Cacodylic acid, alcargen, $\text{HO, C}_4\text{H}_6\text{AsO}_3 = \text{HO} + \text{KdO}_3$.—Cacodyl and its oxide left under water to the slow action of air, oxidate so as to become cacodylic acid. The hydrated acid crystallizes in large colourless prisms, is inodorous, not poisonous, fusible, soluble in water and in alcohol. It is reduced to the state of chloride of cacodyl by chloride of zinc, and to the state of oxide of cacodyl by phosphorus acid. Alcargen has a feeble acid reaction; it combines with the alkalies, giving rise to compounds which have the aspect of gum and are not obtained under regular forms. It dissolves in the hydrate of sulphuric acid without being modified; is not attacked by anhydrous sulphuric acid, and is oxidated with difficulty by nitric acid and aqua regia.

M. Bunsen adds one atom of oxygen to the formula for alcargen, but Liebig has shewn that the formula as given above is more in accordance with Bunsen's analysis of alcargen than his own view.

Sulphuret of cacodyl, $\text{C}_4\text{H}_6\text{As} + \text{S} = \text{KdS}$, may be obtained directly by uniting cacodyl with 1 atom of sulphur, or by the distillation of chloride of cacodyl with sulphuret of potassium.

This body is also a product of the decomposition of oxide of cacodyl by sulphuretted hydrogen gas. It is an ethereal liquid, of a highly disagreeable smell, which does not fume in air, is heavier than water and insoluble in that liquid. The density of its vapour is by experiment 7810, by calculation 8390, its combining measure 2 volumes. It is resolved by hydrochloric acid, into sulphuretted hydrogen and chloride of cacodyl.

Persulphuret of cacodyl of the composition $2C_4H_6As + 5S = 2Kd + 5S$, is formed when sulphur is dissolved in the preceding compound or in cacodyl itself. It may be crystallized from ether in colourless prisms, which fuse at 109.4° (43° cent.) A *protoseleniuret of cacodyl* has also been formed.

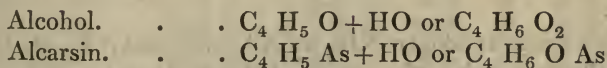
Chloride of cacodyl, $C_4H_6As + Cl = Cd + Cl$, is formed by the digestion of oxide of cacodyl in hydrochloric acid, or by the slow action of chlorine on cacodyl. It is a colourless ethereal liquid, which does not fume in air, does not solidify at -49° (-45° cent.), and is converted a little above 212° into a colourless vapour, which inflames in the air. Its odour is extremely penetrating and stupifying. The density of its vapour is by experiment 4560, by calculation 4860; its combining measure 2 volumes. Chloride of cacodyl combines with metallic chlorides.

Similar compounds of cacodyl with *bromine*, *iodine*, and *fluorine* have been formed.

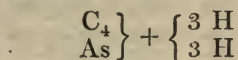
Oxichloride of cacodyl, $KdO + 3KdCl$, is formed by treating the chloride with water, or by distilling it with hydrochloric acid. The density of its vapour is by experiment 5460, by calculation 5300; its combining measure 3 volumes. It is a liquid very like the oxide, boiling at 228.2° (109° cent.) A corresponding *oxibromide of cacodyl* and an *oxyiodide of cacodyl* have been formed.

Cyanide of cacodyl, $C_4H_6As + NC_2 = KdCy$, is produced by the distillation of concentrated hydrocyanic acid or of a solution of cyanide of mercury with oxide of cacodyl. It crystallizes in fine prisms of a diamond lustre, highly limpid, which emit a strong and insupportable odour. It is insoluble in water, fusible at 91.4° (33° cent.) and crystallizable by cooling. Its density in the state of vapour is 4650 by experiment, and 4540 by calculation; its combining measure 2 volumes. The cyanide is the most poisonous of the compounds of cacodyl.

It will be observed that oxide of cacodyl or alcarsin corresponds in composition with alcohol, if As is supposed equivalent to O.



But as alcarsin is the oxide of a radical cacodyl, $\text{C}_4 \text{ H}_6 \text{ As}$, pursuing the analogy, alcohol should be the oxide of a corresponding radical $\text{C}_4 \text{ H}_6 \text{ O}$. Chemists will wait with interest for the investigations of M. Bunsen, illustrative of this point. In the meantime a doubt may be entertained whether the arsenic in alcarsin replaces the oxygen of alcohol, or whether there is any close relation between these two compounds. Their primary binary, or molecular structure is possibly very different. In the ether constituent of alcohol we have probably 4 C zincous or positive, and 5 H + O chlorous. While in cacodyl, we have 4C + As zincous, and 6H chlorous; so that placing the zincous constituent to the left (as usual) and the chlorous to the right, we have the molecular formula for cacodyl as follows :



Cacodyl is thus represented as an association of acetyl and arseniatted hydrogen, forming together a compound radical, which is combined in alcarsin, with 1 atom of oxygen and in alcargen with 3 atoms of oxygen.

SECTION VIII.

ON THE RELATION BETWEEN THE ETHYL AND AMMONIUM SERIES.

A remarkable and highly interesting parallelism exists between these two series of compounds, to which the attention of chemists was first directed by Dr. Kane. It will be observed that acetyl has the relation to ethyl, which amidogen has to ammonium, the more compound radical in both cases containing 2 atoms more of hydrogen than the simpler. We may suppose the ethyl compounds to contain acetyl, as the ammonium compounds are supposed, on one view, to contain amidogen; and when thus resolved the analogy of many of the ethyl to ammonium compounds is very striking. The principal diffe-

rence between the two series depends upon a chemical difference in the characters of their radicals; acetyl being capable of forming acids, while amidogen does not possess that property.

Expressing amidogen NH_2 by Ad, and acetyl C_4H_3 by Ac, the following pairs of compounds from the two series will be found to correspond in composition, differing only in the one containing acetyl while the other contains amidogen. (Liebig's *Traité*).

TABLE OF CORRESPONDING COMPOUNDS.

COMPOUNDS OF ACETYL.		COMPOUNDS OF AMIDOGEN.	
Ac C_4H_3	= acetyl	Ad N H_2	= amidogen
Ac H	= olefant gas	Ad H	= ammonia
Ac H_2	= ethyl	Ad H_2	= ammonium
Ac H_2O	= ether	Ad H_2O	= oxide of ammonium
Ac H_2Cl	= chloride of ethyl	Ad H_2Cl	= chloride of ammonium
Ac H_2Br	= bromide of ethyl	Ad H_2Br	= bromide of ammonium
Ac H_2I	= iodide of ethyl	Ad H_2I	= iodide of ammonium
Ac $\text{H}_2\text{O} + 1 \text{ at. of acid.}$	= salts of oxide of ethyl	Ad $\text{H}_2\text{O} + 1 \text{ at. of acid}$	= salts of oxide of ammonium
Ac $\text{H}_2\text{O} + \text{HO}$	= alcohol	Ad $\text{H}_2\text{O} + \text{HO}$	= compound contained in sulphate of ammonium
Ac $\text{H}_2\text{S} + \text{HS}$	= sulphhydrate of sulphuret of ethyl (mercaptan)	Ad $\text{H}_2\text{S} + \text{HS}$	= sulphhydrate of sulphuret of ammonium
Ac $\text{H}_2\text{O} + \text{CS}_2$	= xanthic acid	Ad $\text{H}_2\text{S} + \text{CS}_2$	= sulphocarbonate of ammonium
Ac $\text{Pt} + \text{Pt Cl}_2$	= compound of platinum of Zeise (acid)	Ad $\text{Hg} + \text{Hg Cl}$	= white precipitate of mercury
Ac, 2Pt Cl + K Cl	= <i>id.</i> with chloride of potassium	Ad, Pt Cl + Ad H_2O	= base of the platinum salts of Gros
Ac 2Pt Cl + Ad H_2Cl	= <i>id.</i> with sal ammoniac	Ad, Pt Cl + Ad H_2Cl	= hydrochlorate of that base
Ac H	= hyduret of acetyl	Ad H	= hyduret of amidogen
Ac H + 2SO	= sulphacetylic acid	Ad H + SO_3	= anhydrous sulphate of ammonium of Rose

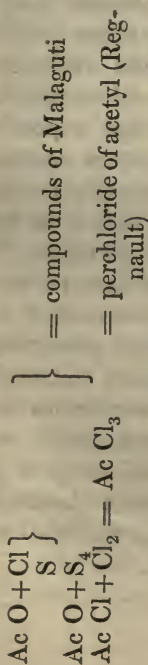
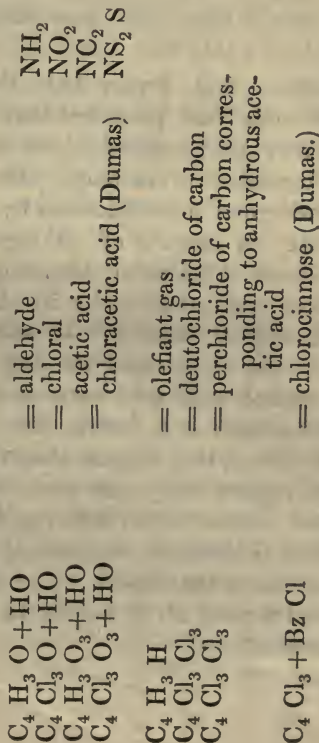
COMPOUNDS OF AMIDOGEN.

COMPOUNDS OF ACETYL.

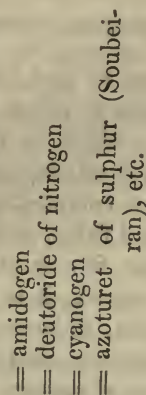
Ac O	= oxide of acetyl	
Ac Cl	= chloride of acetyl	
Ac Br	= bromide of acetyl	
Ac O + HO	= hydrate of the oxide of acetyl (aldehyde)	
Ac Cl + H Cl	= chlorhyd. of chlor. of acet. (Dutch liquid)	
Ac Br + H Br	= bromhydrate of bromide of acetyl	
Ac Cl + Pt Cl	= chloroplatinate of chloride of acetyl (Zeise)	
4Ac + CO	= ?*	Ad + CO = carbamide 2Ad + 2CO = urea Ad + 2CO = oxamide Ad + Bz = benzamide Ad Bz + C ₄ HO ₃ + HO = hippuric acid
Ac + Bz	= oil of cinnamon (Dumas)	
Ac Bz + NO ₅ + HO	= nitrate of oil of cinna- mon	
Ac H ₂ O + 2C ₂ O ₃	= binoxalate of oxide of ethyl	
Ac H ₂ Ad + 2C ₂ O ₃	= oxamethane (Dumas)	
Ac O + O	= aldehydic acid	
Ac O + O ₂ = Ac O ₃	= acetic acid	

* Ac CO = camphor of the oil of cloves (Dumas) ? santonine (Ettling). Ac, 2CO = mannite = C₃ H₃ O + 4HO. Caffein, asparagin, and several other substances also arrange themselves in the series of acetyl.

COMPOUNDS OF ACETYL.

*Substitutions of the hydrogen of acetyl by chlorine.*

COMPOUNDS OF AMIDOGEN.

Substitution of the hydrogen of amidogen.

SECTION IX.

LACTIC AND VISCOUS FERMENTATIONS.

At a temperature between 86 and 104°, the saccharine juices of plants containing albumen or other azotised matter, undergo a species of fermentation, which is different from the vinous, combustible gases being evolved with carbonic acid, and a gummy matter formed, having the composition of gum arabic, which renders the liquid ropy and thick, and hence the application of the name viscous to this fermentation. On examining the liquid after effervescence ceases, it is found to contain no alcohol, but two new substances, in large quantity, namely mannite and lactic acid, which together contain the elements of dried grape sugar, minus 1 atom of oxygen:



MM. Boutron and Fremy have lately observed that the formation of lactic acid precedes that of the other products, and that it may be produced alone, without the evolution of any gas or formation of mannite. Diastase and caseum after they have undergone a modification by a few days' exposure in a humid state, to air, are of all organic matters containing nitrogen the most efficient in determining the lactic fermentation. Air does not interfere by its elements, unless in transforming the animal matter into the lactic ferment. The membranes of the stomach of the dog and calf have no action, when well washed with cold water and fresh, on neutral substances, such as sugar and dextrin, but after being preserved for some time in water, they acquire then the property to transform such matters rapidly into lactic acid. These membranes sometimes produce another acid, differing from the lactic, of which the salt of lime is insoluble in alcohol, while the lactate of lime is readily soluble in that liquid. The substance of bladder after being exposed humid till it begins to decompose, also excites the lactic fermentation.

Diastase after being exposed two or three days to humid air undergoes a modification, and acquire the property of transforming starch into lactic acid, making it pass probably through the intermediate state of dextrin. Hence malt, slightly moistened and exposed to air for two or three days, when afterwards pounded and placed in water kept at a temperature of from 68° to 77° , becomes warm, and after a few days, the liquid is found to contain much lactic acid. This is a pure lactic fermentation, without any production of mannite. But animal matters prepared in a similar manner often modify sugar quite differently, very little lactic acid is formed but considerable quantities of mannite and the viscid matter. Frequently indeed the sugar is wholly changed into alcohol and carbonic acid. The albuminous ferments in different stages of decomposition produce different fermentations. (*Annales de Chimie, &c., 3 série, ii, 257.*)

LACTIC ACID.

Formula of the acid combined with oxide of zinc:

$C_6H_5O_5 = \bar{L}$; of the hydrated acid $HO + C_6H_5O_5 = HO\bar{L}$;
of the sublimed acid $C_6H_4O_4$.

Other sources of lactic acid, are the whey of milk, in which it is formed while the latter becomes sour, human urine, and probably most other animal fluids, the juice of fermented cabbage or sour-cROUT, and the fermented extracts of rice and of nux-vomica, the spent ley of tanners, and the sour water of the starch manufacture, from which lactic acid has been prepared for sale.

The process for lactic acid recommended by Boutron and Fremy consists in mixing 8 or 12 pints of milk, with a solution of 8 or 12 ounces of milk sugar in water, and leaving the liquid exposed to air in an open vessel for several days, between 68° and 77° . The liquid being now found very acid, is neutralised with bicarbonate of soda; after twenty four or thirty hours, being again acid, it is saturated, and the saturation repeated till all the milk sugar is converted into lactic acid. When it is supposed that the transformation is complete, the milk is boiled to coagulate the caseum; and the liquid filtered and evaporated to a syrupy consistence, with caution at a moderate temperature. The product of the evaporation is

taken up by alcohol at 100°, which dissolves the lactate of soda. Sulphuric acid added in proper quantity to the alcoholic solution, forms sulphate of soda, which precipitates, and the liquid yields by evaporation lactic acid nearly pure. To purify the acid, it may be converted into lactate of lime, which crystallizes immediately in tufts which are perfectly white. From this salt lactic acid may be again separated by means of sulphuric acid. Or, the original lactic acid may be saturated with any other base, and crystallized lactates obtained in a very short time.

Concentrated to a maximum by evaporation, lactic acid is a thick, colourless, uncrystallizable liquid, of density 1.215, without smell, and having a strong sour taste, which is scarcely sensible when the acid is dilute. It is soluble in water and alcohol. Lactic acid dissolves the phosphate of lime, a property which some acids, particularly the acetic, do not possess; it coagulates milk when warmed. When heated to 482° (250° cent.), it undergoes a decomposition, water and several other secondary products appearing, but the principal product being a white crystalline sublimate, of which the composition is $C_6H_4O_4$; that is, anhydrous lactic acid minus 1 atom of water.

This new acid may be purified by dissolving the sublimate in boiling alcohol, from which it precipitates on cooling, in the form of rhomboidal tables, of a brilliant whiteness, which have a weak sour taste, are fusible at 224.6° (107° cent.), and sublime at 482° without alteration. These crystals are very slowly soluble in cold water, but dissolve easily in boiling water; the acid then assumes 2 atoms of water and returns to the condition of hydrated lactic acid.

In the lactates, the single atom of basic water only of the formula is replaced by a metallic oxide; no acid lactates are known, but some basic salts of zinc and the magnesian metals appear to exist, which have not been studied. They are all soluble in water; lactate of zinc is the most sparingly soluble.

Lactates.—No lactate of *oxide of ethyl* has been formed. The lactates of *potash*, *soda* and *ammonia* are deliquescent, and do not affect a regular form. The lactate of *barytes* is similar. Lactate of *lime* exists to the extent of 2 or 3 per cent in *nux vomica*. It crystallizes in colourless needles radiating from a centre, which contain 5 atoms of water of crystallization. Lactate of *zinc* is crystallized by the cooling of a boiling solution,

in four-sided prisms, terminated by summits truncated obliquely; they contain 3 atoms of water. Alcohol produces in the aqueous solution a white precipitate of a basic salt, which dissolves in water and crystallizes; it appears to contain 3 atoms of oxide of zinc. Lactate of *magnesia* crystallizes in small plates, containing 3 atoms of water; it dissolves in 30 parts of cold water. The lactates of *alumina*, *nickel*, *lead* and *mercury* are very soluble in water, and do not crystallize in a regular form. Lactates of *protoxide of iron*, $\text{FeO}, \bar{\text{L}} + 3\text{HO}$, of *oxide of copper*, $\text{CuO}, \bar{\text{L}} + 2\text{HO}$, and of *silver* are crystallizable.

Lactate of urea was discovered by MM. Cap and Henry in urine. It may be formed artificially by the double decomposition of lactate of lime and oxalate of urea, the oxalate of lime being separated by a filter, and the liquid evaporated by a gentle heat. The evaporation is terminated in vacuo near concentrated sulphuric acid. Lactate of urea crystallizes in colourless hexagonal needles, of a sharp and cooling taste, which are deliquescent. At a moderate heat it enters into fusion, and sublimes without alteration. Lactate of urea differs from the oxalate and nitrate of urea in not containing 1 atom of water of combination which these possess.

SECTION X.

OIL OF GRAIN-SPIRITS OR FOUSEL OIL, AND BODIES DERIVED FROM IT.

AMYL SERIES OF COMPOUNDS.

Amyl, $\text{C}_{10} \text{H}_{11} = \text{Ayl}$; the hypothetical radical of a series of compounds, of which the hydrate of the oxide has long been known as *fousel oil*, or as the *oil of grain-spirits* or *potatoes*, as it is produced in the fermentation of unmalted grain and potatoes, along with alcohol, and distils over with the latter. It has been studied very fully by M. Cahours (An. de Chim. &c. lxx. 81, and lxxv. 193). There is every reason for considering this body as an alcohol, the most striking analogy existing between oil of potatoes and ordinary alcohol. This will be made sufficiently evident by the following table, in which the corresponding compounds of the ethylic and amilic series are compared:

TABLE OF CORRESPONDING COMPOUNDS.

ETHYLIC SERIES.		AMILIC SERIES.	
Alcohol	C_4H_5O, HO	Oil of potatoes	$C_{10}H_{11}O, HO$
Ether	C_4H_5O	Amilic ether	$C_{10}H_{11}O$ (unknown)
Chlorhydric ether	C_4H_5Cl	Chloride of amyl	$C_{10}H_{11}Cl$
Bromhydric ether	C_4H_5Br	Bromide	$C_{10}H_{11}Br$
Iodhydric ether	C_4H_5I	Iodide	$C_{10}H_{11}I$
Sulphovinic acid	$HO.C_4H_5O, S_2O_6$	Sulphoamilic acid	$HO.C_{10}H_{11}O, S_2O_6$
Sulphovinate of barytes	$BaO.C_4H_5O, S_2O_6$	Sulphoamilate of barytes	$BaO.C_{10}H_{11}O, S_2O_6$
Acetic ether	$C_4H_5O, C_4H_3O_3$	Acetate of oxide of amyl	$C_{10}H_{11}O, C_4H_3O_3$
Chlorinated acetic ether	$H_3O, C_4H_3O_3$ C_4Cl_2	Chlorinated ditto	H^9O, C_4H_3O $C_{10}Cl_2$
Olefiant gas (etherene)	C_4H_4	Amilene	$C_{10}H_{10}$
Aldehyde	C_4H_3O, HO	Amilic aldehyde	$C_{10}H_9O, HO$
Acetic acid	$C_4H_3O_3, HO$	Valeric acid	$C_{10}H_9O_3, HO$

HYDRATE OF OXIDE OF AMYL, OIL OF POTATOES, AND OF GRAIN SPIRITS.

Syn. *Fousel oil, amilic alcohol, bihydrate of amylene*; $C_{10}H_{11}O$, HO (Dumas).

In distilling the fermented wash of grain or potato spirits, a milky liquid comes over towards the end of the process, and an oil subsides after a time, which is hydrate of oxide of amyl, mixed with nearly an equal quantity of alcohol and water. To purify the crude product, it is agitated with water several times, left in contact with chloride of calcium for some time, and distilled again. The alcohol and water come off first, and the boiling point of the liquid rises to $269^{\circ}.6$ (132° centig.), when the receiver should be changed, as what then passes over is perfectly pure.

Hydrate of oxide of amyl is a colourless, limpid, oily liquid, of which the odour, at first agreeable, soon becomes rank and nauseous. The inspiration of its vapour occasions spasmodic pains in the chest, with coughing and even vomiting. It burns with a bluish white flame. Its taste is very acrid. It stains paper, but the stain disappears after a time. The density of this liquid is 0.8124 at 59° ; its boiling point $269^{\circ}.6$; the density of its vapour 3147, of which the combining measure contains 4 volumes; it freezes at -2 or -4° in crystalline leaflets. Water dissolves a small quantity of it so as to acquire the odour of the oil; it is miscible in all proportions with acetic acid, alcohol, ether, the fat and essential oils. It may be mixed also with solutions of caustic potash and soda; when heated with hydrate of potash, hydrogen gas is given off, and the valerate of potash formed. When distilled with anhydrous phosphoric acid, it yields a liquid hydrocarbon, to which Cahours has given the name of *amilene*.

Hydrate of oxide of amyl unites directly with bichloride of tin, according to Gerhardt, and forms a crystalline compound, which is decomposed by water.

Chloride of amyl, $C_{14}H_{11},Cl = Ayl\ Cl$. This compound is obtained by distilling equal parts of oil of potatoes and perchloride of phosphorus. In a state of purity, it is a colourless liquid, of a pretty agreeable odour, insoluble in water, boiling about $215^{\circ}.6$ (102° centig.), perfectly neutral to test-paper, and having no action upon a solution of nitrate of silver.

Chlorinated chloride of amyl, $C_{10}H_8Cl_8$. This substance is the ultimate product of the action of chlorine gas upon the oil in a bottle exposed to the sun, and is formed by the substitution of 8 atoms of chlorine for 8 atoms of hydrogen. It is a colourless liquid, of a strong odour, suggesting that of camphor.

Bromide and iodide of amyl were also formed by Cahours. Caustic alkalies dissolved in water attack them with difficulty, but the same bodies dissolved in alcohol decompose these ethers with much facility. The iodide of amyl is produced by distilling at a gentle heat, a mixture of 8 parts of iodine, 15 parts of hydrate of oxide of amyl, and 1 part of phosphorus. The density of its vapour is 6675, and combining measure 4 volumes.

Acid sulphate of oxide of amyl, sulphoamilic acid, is formed when the barytes of the following salt is exactly precipitated by dilute sulphuric acid; it may be evaporated to a syrupy consistence in air or in vacuo, and is sometimes obtained in the form of very fine needles. Its solution is decomposed by heat. When neutralised with bases, it forms a class of salts, the sulphoamylates, which are all soluble in water.

Sulphate of oxide of amyl and barytes, $BaO \cdot AylO \cdot S_2O_6 + 3HO$. This salt is prepared by mixing equal parts of concentrated sulphuric acid and hydrate of oxide of amyl, and neutralising with carbonate of barytes; sulphate of barytes precipitates, while sulphate of amyl and oxide of amyl remains in solution, and may be crystallized by evaporation after being purified by animal charcoal. It forms pearly crystalline leaflets, which are very soluble in water and in alcohol, but scarcely dissolve in ether. The crystals contain 3 atoms of water; when dried at 212° they retain only 2 atoms; the dry salt is decomposed at 392° (200° centig.) Its solution is decomposed by boiling, with escape of hydrate of oxide of amyl.

Sulphate of oxide of amyl and potash forms colourless needles or plates, grouped about a common centre, is very soluble in water and alcohol, and has a very bitter taste.

Sulphate of oxide of amyl and lead crystallizes with 2 atoms of water. Its solution is decomposed by ebullition, like that of the salt of barytes. The salt of *lime* is similar in composition.

Acetate of oxide of amyl, $C_{10}H_{11}O, C_4H_3O_3 = AylO, AcO_3$. It is produced by distilling a mixture of 2 parts of acetate of potash, 1 part of hydrate of oxide of amyl, and 1 part of concentrated sulphuric acid. It is a colourless liquid, of an aromatic and ethereal odour, lighter than water, boiling about 257° ; insoluble in water, but soluble in alcohol, ether, oil of potatoes, etc. Placed in contact with an aqueous solution of potash, it is altered very slowly; an alcoholic solution of the same base, on the contrary, alters it rapidly, an alkaline acetate is produced, and the oil is regenerated. The density of its vapour is 4475, and combining measure 4 volumes.

Chlorinated acetate of oxide of amyl, $C_{10} \frac{H_9}{Cl_2} O + C_4 H_3 O_3$.

This compound is formed when the acetate is saturated with chlorine gas at a temperature increasing to 212° . It is a colourless neutral liquid, insoluble in water; and corresponds in composition with the chlorinated acetic ether of Malaguti. It is a liquid body, which becomes yellow, and is altered by a heat above 302° . When exposed again to chlorine gas in sunshine, this liquid absorbs the gas, and a crystalline product is formed containing more chlorine, but which has not been analysed.

Valeric or valerianic acid, $HO, C_{10}H_9O_3$. Oil of potatoes becomes acid when kept in contact with air. M. Cahours has observed, that if platinum black be heated, and the oil be allowed to fall upon it drop by drop in no greater quantity than is imbibed, oxidation occurs, and an acid liquid volatilises, which has all the properties of valerianic acid, the acid obtained by distillation of the root of valerian (*valeriana officinalis*) with water. Two atoms of hydrogen in the oil are replaced by 2 atoms of oxygen. Oil of potatoes corresponds in this respect with alcohol and wood-spirit, which are converted in similar circumstances, by the substitution of 2 atoms of oxygen for 2 atoms of hydrogen, into peculiar acids, the acetic and formic acids. But valerianic acid was first obtained from the oil by MM. Dumas and Stass, by distilling it with hydrate of potash. One part of the oil was covered in a retort by about 10 parts of a mixture of equal parts of hydrate of potash and quicklime; and distilled by a metallic bath at about 392° (200° centig.); hydrogen gas comes over, and valerate of potash is formed. The mass is

neutralised by a slight excess of sulphuric acid, and distilled to separate the valeric acid. At the same time, a portion of hydrate of oxide of amyl comes over, accompanied by a liquid having the composition of a *valeric aldehyde*.

Obtained from pure valerate of soda, mixed with a slight excess of phosphoric acid, valeric acid is a colourless oil, lighter than water, and possessed of a persistent and characteristic odour which recalls that of the root of valerian, with a sharp and acid taste. The protohydrate produces a white spot on the tongue; its density is 0.937 at 61°·7 (16°·5 centig.); it boils without change at about 347° (175° centig.); it remains liquid at 5°. It inflames easily, and burns with a white and smoky flame. The density of the vapour of this hydrate is 3660 by experiment, 3550 by theory; its combining measure 4 volumes, in which respect it differs from acetic acid. Valeric acid, agrees, however, with that acid in forming a terhydrate, the condition in which valeric acid is always obtained when separated from its salts dissolved in water. Placed in contact with water, valeric acid dissolves a certain quantity of it; the water on its part dissolves the acid considerably.

Valerates.—These salts are in general soluble in water. The valerates of *potash* and *barytes* are not crystallizable. The valerate of *silver* is a heavy crystalline powder, of sparing solubility, which might be confounded, from its appearance, with the fulminate of the same metal.

MM. Dumas and Stass formed two acids by the action of chlorine upon valeric acid, *chlorovalerisic acid*, $C_{10} \overset{H^6}{Cl_3} O_3 + HO$, in which 3 atoms of hydrogen are replaced by 3 atoms of chlorine, and *chlorovalerosic acid*, $C_{10} \overset{H^5}{Cl_4} O_3 + HO$, in which 4 atoms of hydrogen are replaced by 4 atoms of chlorine.—(An. de Chim. lxxiii, 136.)

Amilene, $C_{10}H_{10}$; a liquid hydrocarbon, obtained by distilling hydrate of oxide of amyl repeatedly with anhydrous phosphoric acid. It is colourless, possesses a peculiar aromatic odour, is lighter than water, and contains no oxygen. It boils at 320°; the density of its vapour is 5061 by experiment, and 4900 by calculation, its combining measure 2 volumes.

SECTION XI.

ETHEREAL OIL OF WINES.

The characteristic odour of wine by which it is distinguished from dilute alcohol, is due to a particular substance, possessing the properties of an essential oil. This is common to all wines, and is not to be confounded with the principle which is generally termed the flower, aroma or *bouquet* of individual wines, which is not volatile, and appears to be different in diverse kinds of wine and to be altogether wanting in many kinds.

This oil is less volatile than alcohol, and a small quantity of it is found in the still after the distillation of a large quantity of wine. The same oily liquid is also obtained on distilling the lees of wine, especially what is deposited at the bottom of the tun after the fermentation has begun. It constitutes about $\frac{1}{1000}$ part of wines. This oil belongs to the class of compound ethers, and contains a new acid, which has been named *cœnanthic acid*,* in combination with ether; the oil, therefore falls to be named cœnanthic ether.

Cœnanthic ether, $C_4H_5O, C_{14}H_{13}O_2$. The crude ether contains a variable quantity of free acid in a state of mixture; being more volatile than the acid, the oil may be separated from it by a simple distillation, collecting only the first fourth of the product. To obtain it perfectly pure, it is preferable to agitate the oil frequently with a hot solution of carbonate of soda, which dissolves the free acid without altering the ether. The small quantity of water and alcohol it retains may be withdrawn from it by digestion with chloride of calcium.

The ether purified in this manner, is very fluid, colourless with the odour of wine extremely strong, and almost intoxicating when closely inspired. Its taste is very strong and disagreeable. It dissolves easily in ether and in alcohol, even when the latter is pretty dilute; water does not sensibly dissolve it. Its density is 0.862, its volatility very feeble; it boils between 437 and 446° (225 and 230° centig.); the density of its vapour is by experiment 10508, by calculation 10476.9, its combining measure 2 volumes. Cœnanthic ether is instantly

* From *οἶνος* wine, and *ανθος* flower.

decomposed by caustic alkalies, but is not sensibly affected by alkaline carbonates, nor by ammonia. When boiled with caustic potash, it disappears in a few seconds, a considerable quantity of alcohol distils over, and the liquor contains a compound of œnanthic acid and potash, which is very soluble in water.

œnanthic acid, $\text{HO}, \text{C}_{14}\text{H}_{13}\text{O}_2$. When separated from its alkaline combinations, well washed with hot water and dried, this acid, at $55^{\circ}.7$, is of the consistence of butter and perfectly white, but at a higher temperature it melts and forms a colourless oil, without taste or odour, which reddens litmus, dissolves easily in caustic alkalies and in alkaline carbonates. It dissolves easily in alcohol and ether. This acid, like all the fatty acids, forms two series of salts, one acid in composition, without, however, manifesting a sensible acid re-action, the other neutral in composition, which exhibits a well-marked alkaline re-action.

Hydrated œnanthic acid submitted to distillation abandons its water, and becomes anhydrous, $\text{C}_{14}\text{H}_{13}\text{O}_2$, water and a little of the hydrated acid distilling over. The boiling point of the anhydrous acid is more elevated than that of the hydrated acid, as also is the point of fusion of the former; fused anhydrous œnanthic acid becoming solid about $87^{\circ}.8$ (31° centig.)

œnanthic ether may be reproduced by means of the isolated œnanthic acid. When 5 parts of sulphovinate of potash are heated with 1 part of hydrated œnanthic acid, the mixture fuses; and if it is heated to 302° (150° centig.), an oily liquid is seen to form on its surface, which is a mixture of œnanthic ether and œnanthic acid still free. If this oily layer be separated and heated with a solution of carbonate of soda, the free acid is dissolved and the ether remains in a state of purity.

CHAPTER III.

PRODUCTS OF THE DRY DISTILLATION OF WOOD.

The principal products of the destructive distillation of wood at a red heat, are the charcoal which remains in the retort,

gaseous compounds of carbon, a watery fluid containing acetic acid, and a black odorous oily mass, known as tar. The two last products are highly variable mixtures of a great many substances, of which the one that demands our first attention is pyroxylic spirit, or wood spirit.

SECTION I.

METHYL SERIES OF COMPOUNDS.

Formula of methyl, $C_2H_3=Me$.

A volatile combustible spirit, soluble in water, was first obtained from the dry distillation of wood by Mr. P. Taylor. The composition and chemical nature of this spirit and of the compounds it forms, with their extraordinary parallelism to alcohol and the compounds derived from alcohol, were ascertained by MM. Dumas and Peligot, and published in their important memoir on wood-spirit (*An. de Ch.* lviii, 5). Wood-spirit is the alcohol of a particular series of compounds, being the hydrated oxide of a new radical methyl, which resembles ethyl perfectly in its functions, but differs in its composition, containing 2 atoms less of carbon and 2 atoms less of hydrogen. The oxide of methyl is a base like the oxide of ethyl or ether, and forms acid and neutral salts like the latter. By the abstraction of 2 atoms of hydrogen from methyl, another radical formyl is produced, as acetyl is derived from ethyl, and having an acid oxide formic acid, corresponding with acetic acid. Methyl has not been isolated.

OXIDE OF METHYL.

Formula $C_2H_3O=MeO$.

Syn. *Methylic ether*.—This compound is prepared by distilling wood spirit with 4 parts of sulphuric acid, and transmitting the gas which comes over first through a bottle containing milk of lime and afterwards through several bottles filled with pure water. The latter dissolves the oxide of ethyl; the gas is evolved on boiling its solution, and must be collected over mercury. Oxide of methyl is a colourless gas of an agreeable ethereal odour, not liquified by a cold of $+3^{\circ}.2$ (-16° cent.),

and combustible; water dissolves 37 volumes of this gas, alcohol, hydrate of oxide of methyl and concentrated sulphuric acid much larger proportions. It separates from the latter, on dilution with water; the density of the gas is by experiment 1605, by calculation 1570, and its combining measure 2 volumes.

Oxide of methyl combines directly with the vapour of anhydrous sulphuric acid, in a glass balloon carefully cooled, and forms the neutral sulphate of oxide of methyl (Regnault).

HYDRATE OF OXIDE OF METHYL, OR WOOD SPIRIT.

Formula, $C_2H_3O + HO = MeO + HO$.

Syn. *Pyroxylic spirit*.—In the process of purifying the vinegar from wood, the crude acid is saturated with lime and concentrated by evaporation. The first portion of liquid which distils over contains the wood spirit, which is concentrated by repeated rectification. The wood spirit or pyroxylic spirit of commerce is a heterogeneous mixture, containing besides the hydrate of oxide of methyl which forms the larger part of it, acetone and several other combustible liquids. To purify the wood spirit it is poured over an excess of chloride of calcium in a retort, and distilled by a water-bath heat, which expels acetone and other liquids and leaves the wood spirit united with the chloride of calcium. A measure of water equal to the original volume of the wood spirit is then added to the retort, and the distillation continued; the latter liquid comes over diluted with a small quantity of water, from which it may be separated and obtained anhydrous by another distillation from quicklime.

Wood spirit is a volatile colourless liquid, of an alcoholic but at the same time empyreumatic smell and taste. It is very inflammable and burns with a pale flame like alcohol. It is neutral, mixes when pure with water, without becoming turbid, and is also miscible with alcohol and ether. Its density is 0.798 at 68°; it boils at 140° according to Kane, and at 151°.7 (66°.5 cent.) according to Dumas. The density of its vapour is by experiment 1120, by calculation 1110; its combining measure 4 volumes.

Hydrate of oxide of methyl dissolves, with the aid of heat,

small portions of sulphur and phosphorus; it dissolves also many resins, and is used in making spirit varnishes, and mixes with most volatile oils; its solvent power is indeed very similar to that of alcohol. Wood spirit is acted upon by chlorine, peroxide of manganese and sulphuric acid and by other oxidating agents, like alcohol, yielding analogous products. It is also decomposed by potassium, with disengagement of pure hydrogen.

Anhydrous *barytes* is dissolved by pure wood spirit with evolution of much heat, although not dissolved by alcohol, and a compound formed $\text{MeO}, \text{HO} + \text{BaO}$, which crystallizes in needles of a silky lustre. Wood spirit likewise dissolves lime.

Chloride of calcium dissolves in wood spirit and crystallizes from a strong solution in large hexagonal tables, which deliquesce in air; they contain 2 atoms of hydrate of oxide of methyl united with 1 atom of chloride of calcium. Dr. Kane recommends the decomposition of this salt by heat as the best source of pure wood spirit.

Chloride of methyl, $\text{C}_2\text{H}_3\text{Cl} = \text{MeCl}$.—This compound is produced by the reaction of hydrochloric acid and hydrate of oxide of methyl upon each other:



But it is best obtained, as are all the halogen compounds of methyl, by distilling neutral sulphate of oxide of methyl with a metallic salt of the proper salt radical, or better a mixture of sulphuric acid, hydrate of oxide of methyl and the metallic salt. The salt used in the present case is chloride of sodium. Chloride of methyl is a colourless gas of an ethereal odour and sweet taste, of which the density is 1737.8 by experiment, and 1729 by calculation; the combining measure is 4 volumes. Water dissolves 2.8 volumes of this gas at $60^\circ.8$ (16° centig.); it is not liquified by a cold of -0.4° (-18° centig.) It will be remarked that the chloride and oxide of methyl are both considerably more volatile than the chloride and oxide of ethyl.

Iodide of methyl, MeI ; a colourless liquid, which burns with

difficulty, boiling between 104° and 122° ; its density is 2.237 at 69.8° (21° centig.)

Fluoride of methyl, MeF ; obtained by distilling sulphate of oxide of methyl with fluoride of potassium; a colourless gas, of which the density is 1186; water dissolves 1.5 volumes of it.

Cyanide of methyl, MeCy ; an ethereal liquid, insoluble in water.

Sulphuret of methyl, MeS ; a very limpid liquid of which the odour is extremely disagreeable. Its density is 0.845 at $69^{\circ}.8$, and its boiling point $105^{\circ}.8$ (41° centig.) The density of its vapour is by experiment 2115, by theory 2158; its combining measure 2 volumes. Sulphuret of methyl is formed, when chloride of methyl is transmitted through an alcoholic solution of protosulphuret of potassium, by double decomposition.

Sulphydrate of sulphuret of methyl or methylic mercaptan is obtained as a colourless liquid, lighter than water, which boils at $69^{\circ}.8$ and acts upon oxides of mercury and lead like sulphhydrate of sulphuret of ethyl (Gregory).

OXYGEN SALTS OF METHYL.

The salts of oxide of methyl correspond so closely with those of ethyl that knowing the history of one class it is easy to predict the properties of the other. Anhydrous metallic oxides do not alter them, while the hydrated alkalies disengage hydrate of oxide of methyl from them with great facility.

Neutral sulphate of oxide of methyl, MeO, SO_3 .—This member of the methyl series, which has no analogue in the ethyl series, is formed when oxide of methyl and anhydrous sulphuric acid are brought into contact. It constantly appears also when hydrate of oxide of methyl is distilled with sulphuric acid, and in larger quantity the greater the proportion of sulphuric acid employed. To prepare sulphate of methyl it is convenient to distil 1 part of hydrate of oxide of methyl with 8 or 10 parts of sulphuric acid. When purified by washing with water, and two successive distillations with chloride of calcium and quicklime, sulphate of methyl is a colourless liquid of an alliaceous odour, of density 1.324 at $71^{\circ}.6$ (22° centig.), which boils at $370^{\circ}.4$ (188° centig.), and may be distilled without change. The density of its vapour is 4363.4; it is composed of equal volumes

of anhydrous sulphuric acid and oxide of methyl condensed into one volume, so that its combining measure is the same as that of oxide of methyl or 4 volumes. It is decomposed very slowly by cold water, but rapidly by hot water, the acid sulphate of oxide of methyl and water being formed and oxide of methyl liberated. This compound may be employed in preparing all the other compounds of methyl, which are derived from it by double decomposition.

Acid sulphate of oxide of methyl, bisulphate of oxide of methyl, sulphomethylic acid; $\text{HO} \cdot \text{MeO} + \text{S}_2\text{O}_6$.—This compound, discovered at the same time by MM. Dumas and Peligot and by Dr. Kane, is formed when concentrated sulphuric acid is mixed with hydrate of oxide of methyl, and also on dissolving the neutral sulphate in boiling water. Obtained by the last method and concentrated by evaporation it is a colourless, syrupy, very acid liquid which in dry air becomes a mass of white crystalline needles. It combines with bases forming double salts, in which the basic water of the acid is replaced by a metallic oxide. All these salts are soluble in water. The double salt of *oxide of ammonium and oxide of ethyl* has not yet been obtained.

Sulphate of oxide of methyl and potash, $\text{MeO} \cdot \text{KO} \cdot \text{S}_2\text{O}_6 + \text{HO}$ crystallizes in rhomboidal tables, which have the lustre of mother of pearl and deliquesce in damp air. Dr. Gregory has obtained two double salts by dissolving the present salt in a saturated solution of ferrocyanide of potassium, and evaporating; the first which crystallizes yellow and insoluble in alcohol, is a compound of ferrocyanide of potassium and ferrocyanide of methyl; the second a white salt soluble in alcohol is a compound of sulphate of oxide of methyl and potash, bisulphate of potash and cyanide of methyl.

Sulphate of oxide of methyl and barytes, $\text{MeO} \cdot \text{KO} \cdot \text{S}_2\text{O}_6 + 2\text{HO}$; is prepared by mixing equal parts of concentrated sulphuric acid and hydrate of oxide of methyl, and heating the mixture to its boiling point. After cooling, the liquid is diluted and saturated first with carbonate of barytes and afterwards with hydrate of barytes; the excess of the latter is removed by a stream of carbonic acid gas, and the liquid evaporated to its crystallizing point by a gentle heat. The salt crystallizes in colourless tables of a square base or in thin transparent plates, which effloresce in air and may be made anhydrous in vacuo.

Sulphate of oxide of methyl and lead, $\text{PbO} \cdot \text{MeO} \cdot \text{S}_2\text{O}_6 + \text{HO}$,

is deliquescent. It has likewise been obtained with 2 atoms of water of crystallization and the same form as the preceding salt of barytes (Kane).

Nitrate of oxide of methyl, MeO, NO_5 .—The action of nitric acid upon wood spirit is different and much less violent than the action of the same acid upon alcohol. No nitrate of oxide of ethyl is formed, indeed such a compound does not appear to exist, while the nitrate of oxide of methyl is very easily obtained. One part of nitrate of potash and a mixture of 2 parts of concentrated sulphuric acid with 1 part of wood spirit are introduced into a retort; the mass rises greatly in temperature, and the product distils over without the necessity for applying artificial heat; it must be received in a very cold condenser. The heavier of the two liquids found in the receiver is nitrate of oxide of methyl contaminated with a portion of a very volatile compound supposed to be formiate of oxide of methyl, which communicates to the former the odour of hydrocyanic acid. The product is rectified from chloride of calcium and from litharge; the last portions which distil over are perfectly pure. Nitrate of oxide of methyl is a colourless liquid of a weak ethereal odour, which inflames with facility and burns with a yellow flame; its density is 1.822 at $71^\circ.6$ (22° centig.), and boiling point $150^\circ.8$ (66° centig.) Its vapour heated above 248° is decomposed with a violent detonation, producing carbonic acid, water and deutoxide of nitrogen. This ether is soluble in water, and miscible in all proportions with alcohol, ether and wood spirit.

Neutral carbonate of oxide of methyl is unknown; the *double carbonates* which it forms with alkaline carbonates were prepared in the same manner as the corresponding double salts of ethyl.

Oxalate of oxide of methyl, $\text{MeO}, \text{C}_2\text{O}_3$, is a white solid transparent and brilliant mass composed of rhomboidal tables; it fuses at $123^\circ.8$ (51° centig.), and boils about $321^\circ.8$ (161° centig.) It is decomposed by water and resolved into hydrated oxalic acid and wood spirit. *Acid oxalate of oxide of methyl* has not yet been obtained.

Oxalate of oxide of methyl and oxamide or *oxamethylane* is formed when oxalate of oxide of methyl is exposed to dry ammonia.

Sulphocarbonate of oxide of methyl and potash, $\text{KO.MeO}, \text{C}_2\text{S}_4$.

Bicyanurate of oxide of methyl, $3 \text{ MeO}, \text{Cy}_6\text{O}_6 + 6\text{HO}$, (Richardson).

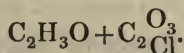
Benzoate of oxide of methyl, $\text{C}_2\text{H}_3\text{O}, \text{C}_{14}\text{H}_5\text{O}_3 = \text{MeO}, \text{BzO}$.

Acetate of oxide of methyl, $\text{C}_2\text{H}_3\text{O}, \text{C}_4\text{H}_3\text{O}_3 = \text{MeO}, \text{AcO}_3$.

Mucate of oxide of methyl, $2\text{C}_2\text{H}_3\text{O}, \text{C}_{12}\text{H}_{14}\text{O}_7 = 2\text{MeO} + \text{Mu}$, (Malaguti).

COMPOUNDS OF OXIDE OF METHYL OF AN UNCERTAIN CONSTITUTION.

Oxichlorocarbonate of oxide of methyl, $\text{C}_4\text{H}_3\text{ClO}_4$; considered by MM. Dumas and Peligot as a compound of oxide of methyl, and a particular acid, and represented by the formula :



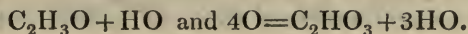
Urethylane, a body corresponding with urethane and formed in similar circumstances.

Sulphate of oxide of methyl and sulphamide, or sulphamethyllane, $\text{C}_2\text{H}_3\text{O}, \text{SO}_3 + \text{NH}_2, \text{SO}_2$.

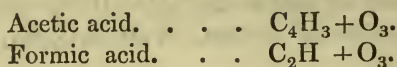
PRODUCTS OF THE DECOMPOSITION OF METHYL AND ITS DERIVATIVES.

A compound belonging to the methyl series was obtained by MM. Dumas and Peligot, which appears to correspond with isethionic acid, by bringing anhydrous sulphuric acid in contact with hydrate of oxide of methyl, observing to keep the mixture cool. Its salt of barytes is crystallizable and has the same composition as sulphate of oxide of methyl and barytes, but does not agree with the latter in its chemical properties, and is evidently a different substance.

Under the influence of air, hydrate of oxide of methyl in contact with platinum black undergoes oxidation, and forms an acid, which is found to be pure formic acid. In this conversion, 2 atoms of hydrogen combine with oxygen and form water, and 2 atoms of oxygen are absorbed at the same time, and combine with the remaining elements of the methyl, exactly as in the conversion of alcohol into acetic acid :



Formic acid therefore contains a radical, which is named formyl, and to which it has the same relation as acetic acid has to acetyl:



Formyl therefore differs from methyl in containing 2 atoms less of hydrogen, and as ethyl may be viewed as a compound of acetyl + 2 atoms of hydrogen, so methyl may be viewed as a compound of formyl + 2 atoms of hydrogen.

SECTION II.

FORMYL SERIES OF COMPOUNDS.

Formyl, $\text{C}_2\text{H}=\text{Fo}$.

The series of formyl is less numerous than that of acetyl. The compounds of the former corresponding to aldehyde and aldehydic acid are deficient, formic acid being the only known oxide of formyl.

The following are the derivatives of formyl:

C_2HO	Oxide of formyl (unknown).
$\text{C}_2\text{HO} + \text{HO}$	Substance contained in formomethylal.
C_2HO_3	Anhydrous formic acid.
$\text{C}_2\text{HO}_3 + \text{HO}$	Hydrated formic acid.
C_2HCl_3	Perchloride of formyl (chloroform).
C_2HBr_3	Perbromide of formyl.
C_2HI_3	Periodide of formyl.

COMPOUND OF HYDRATE OF OXIDE OF FORMYL WITH OXIDE OF METHYL, OR METHYLAL.

Syn. *Formomethylal* (Kane) $\text{C}_6\text{H}_8\text{O}_4$ (Malaguti).

By distilling 2 parts of wood spirit with 3 parts of sulphuric acid diluted with 3 parts of water, and 2 parts of peroxide of manganese, Dr. Kane obtained a substance mixed with several other bodies, which he named formomethylal. It was considered a tribasic formiate of oxide of methyl, but was after-

wards shown by Malaguti, to be a mixture of formiate of oxide of methyl and a particular substance which he named methylal. To purify the methylal from formiate of oxide of methyl, the latter must be decomposed entirely by hydrate of potash.

Methylal is an ethereal colourless liquid of a very agreeable aromatic odour; it is miscible with 3 parts of water, and may be separated from that liquid by chloride of calcium or hydrate of potash. It is very inflammable, and burns with a white flame. The density of methylal is 0.8551; its boiling point 107.6° (42° centig.); its combining measure contains 4 volumes. Methylal may be represented as a compound of 1 atom of hydrate of oxide of formyl with 2 atoms of oxide of methyl $=C_2HO, HO + 2C_2H_3O$. M. Regnault has explained its formation by supposing that 3 atoms of oxide of methyl, formed by the action of sulphuric acid upon hydrate of oxide of methyl, group together so as to form a single molecule $=C_6H_9O_3$; the last exposed to the oxidating action of peroxide of manganese loses 1 atom of hydrogen, which is replaced by 1 atom of oxygen, and consequently the compound $C_6H_8O_4$ is produced. The formation of *acetal* which corresponds with methylal in the acetyl series is explained by Regnault in the same manner.

FORMIC ACID.

Formula $HO + C_2HO_3 = HO, FoO_3$.—The relation of this acid to wood spirit has already been explained. It was distinguished as a particular acid by Gehlen, who found it in red ants (*formica rufa*); and was first formed artificially by Dœbereiner, by distilling tartaric acid with sulphuric acid and peroxide of manganese. All other vegetable substance when oxidised in the same manner, or by distillation with nitric acid, hyperiodic, iodic and hypermanganic acids, or with a mixture of chromic and sulphuric acids, yield formic acid, carbonic acid and occasionally some acetic acid.

To obtain the protohydrate in a state of purity, formiate of lead well pulverised contained in a long glass tube is decomposed by a current of dry sulphuretted hydrogen gas; and the disengaged formic acid afterwards distilled over by the application of a gentle heat. This hydrate is a colourless liquid, slightly fuming and possessing a pungent and peculiar odour. It

crystallizes below 32° in brilliant plates; it boils at 212° ; its density is 1.2353. The vapour of the boiling acid is inflammable and burns with a blue flame; this hydrate combines with a second atom of water forming a definite compound of which the boiling point is 222.8° (106° centig.), which does not freeze at 5° , and of which the density is only 1.1104 at 59° . Both of these hydrates are highly corrosive.

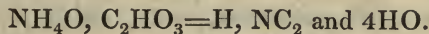
To prepare the dilute acid, a capacious glass retort or copper still is employed, of which the capacity must be at least 10 times greater than the volume of the materials to be employed, namely 1 part of starch, 4 parts of peroxide of manganese, 4 parts of water, and 4 parts of sulphuric acid. The materials without the acid are first introduced into the retort and heated to 104° (40° centig.), and then the sulphuric acid is added by small portions. A violent effervescence with swelling up of the materials occurs, from the disengagement of carbonic acid gas; when this ceases and all the acid is added, the capital is applied to the still, and the distillation continued, for which a heat a few degrees above 212° is sufficient, till $4\frac{1}{2}$ parts of the liquid are found in the receiver. The product is a dilute acid, of which the density is about 1.025; the last portions often contain sulphurous acid, and the product has always an aromatic odour from the presence of a small quantity of a volatile oil formed in the process. The nature of the decomposition which yields formic acid has not been exactly traced. To purify the crude formic acid it is neutralised by milk of lime, which forms an insoluble compound with sulphurous acid; the excess of lime is precipitated by a stream of carbonic acid and the formiate of lime evaporated to dryness. By distilling 10 parts of formiate of lime with 8 parts of oil of vitriol diluted with 4 parts of water, 9 parts of a pure acid are obtained of specific gravity 1.075.

Formic acid is entirely decomposed by an excess of sulphuric acid, without being charred, being resolved into carbonic oxide which comes off with lively effervescence, and water which remains in combination with the sulphuric acid. The acid in question may easily be recognised by that property and also by its action upon the oxides of silver and mercury. When heated upon these oxides formic acid is completely destroyed, producing carbonic acid gas which is disengaged, water and

metallic silver or mercury, without leaving the smallest trace of a salt of silver or mercury in the liquor. When the formic acid contains acetic acid, acetate of suboxide of mercury remains in solution. Heated with a solution of corrosive sublimate, formic acid reduces the latter to the condition of calomel, disengaging hydrochloric and carbonic acids; upon the salts of oxides of mercury and silver, formic acid has the same action as upon the oxides themselves. Metallic peroxides are reduced by it with the aid of heat to the state of protoxides, which combine with formic acid, while carbonic acid gas is disengaged.

Formiates.—Formic acid is more powerful than acetic acid; the salts of both acids are all soluble in water. Formiate of soda is not soluble in alcohol like acetate of soda; the formiates comport themselves like the free acid, with sulphuric acid; they also when heated in excess with solutions of salts of silver, mercury, platinum or chloride of gold, precipitate these metals, producing a brisk effervescence. The salts of peroxide of iron are coloured deep orange by a formiate.

Formiate of ammonia, NH_4O , FoO_3 , crystallizes in square four-sided prisms; it is very soluble in water. This salt contains the elements of 1 atom of hydrocyanic acid and 4 atoms of water:



It is accordingly converted into these two products when its vapour is carried through a tube at a red heat.

Formiate of oxide of ethyl, formic ether, EO, FoO_3 .—This ether is obtained by distilling 7 parts of dry formiate of soda with a mixture of 10 parts of sulphuric acid and 6 parts of alcohol of 90 per cent. It is a limpid liquid of an aromatic penetrating odour and cooling spicy taste. Its density is 0.912; its boiling point 128.12° (53.4° centig.) Formic ether dissolves in 10 parts of water; ammoniacal gas has no action upon it, while solution of ammonia decomposes it like the other alkalies. *Formiate of oxide of methyl* is lighter than water, and boils between 36 and 38° centigrade; its odour suggests that of acetic ether.

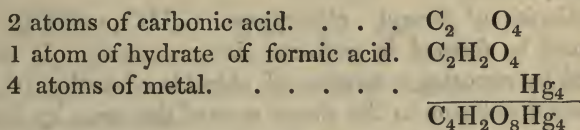
Formiate of potash is very soluble and crystallizes with difficulty. *Formiate of soda* crystallizes in prisms of a rhombic base or in tables, containing 2 atoms of water; it is very soluble and deliquescent in damp air. This salt is very suitable for reducing many metallic oxides, when heated with them to redness in the dry way, or when boiled with their solutions. Its solution may be employed to separate the reducible metals from iron, copper, manganese, &c., which are not deoxidised by formic acid.

Formiate of barytes crystallizes in brilliant transparent prisms, which are persistent in air, soluble in 4 parts of water and insoluble in alcohol. *Formiate of strontian* crystallizes in transparent six-sided prisms, containing 4 atoms of water. *Formiate of lime* is soluble in 10 parts of water, and scarcely more soluble with heat than in the cold, so that the best mode of crystallizing it, consists in evaporating its solution by a gentle heat. A concentrated solution of the salt deposits, by evaporation, needles of a brilliant lustre, which effloresce when heated. *Formiate of magnesia* crystallizes in thin brilliant needles, persistent in air, which are soluble in 13 parts of water and insoluble in alcohol. *Formiate of alumina* gives by evaporation a gummy mass which is not crystalline. Its solution with the addition of sulphate of potash, alum, &c., becomes turbid when heated, like acetate of alumina. *Formiates of manganese, protoxide of iron, zinc, cadmium, nickel, cobalt, and copper* are very soluble and crystallizable salts.

Formiate of cerium is a white granular and crystalline powder; it is the most insoluble formiate, a property of which advantage is taken in preparing pure oxide of cerium from solutions containing oxide of iron, lime and other oxides. At 392° (200° centig.), this formiate enters into a kind of ebullition and is converted into carbonate of cerium, without charring.

Formiate of lead requires 36 or 40 parts of water for solution, and precipitates when formic acid is added to a saturated solution of acetate of lead, in brilliant needles diverging from a common centre. The solution of formiate of lead has a sweet taste, it is capable of dissolving oxide of lead when boiled upon that oxide and acquires an alkaline reaction. *Formiate of lead* is insoluble in alcohol.

Formiates of suboxide and oxide of mercury.—Red oxide of mercury well pounded dissolves in formic acid, at the ordinary temperature and forms a solid crystalline mass on evaporating in dry air, which is the formiate of that oxide. On applying the slightest heat to this salt either dry or in solution, effervescence occurs from the escape of carbonic acid, and formiate of suboxide of mercury is produced. The latter salt is deposited from a solution so decomposed, in a crystalline very brilliant micaceous mass, which is composed of small plates of 4 or 6 sides, of a silky or silvery lustre. By a higher temperature formiate of the suboxide is decomposed whether dry or in solution, with a slight explosion, metallic mercury being liberated with formic and carbonic acids. The decomposition of this salt is thus represented by Liebig: 2 atoms of formiate of suboxide of mercury are resolved by heat into:



Formiate of silver is also a salt of sparing solubility. It is obtained by the double decomposition of nitrate of silver with an alkaline formiate, in small leaflets of brilliant whiteness; it is decomposed by heat and resolved into the metal formic and carbonic acids.

Artificial oil of ants, $\text{C}_5\text{H}_2\text{O}_2$ (Stenhouse).—This name was applied by Döbereiner to the oil which appears in the preparation of formic acid. It was obtained by Dr. Stenhouse in larger quantity than it is produced in the ordinary process, by distilling together equal weights of oatmeal or sawdust and sulphuric acid diluted with its own bulk of water. In the process for formic acid the peroxide of manganese cannot be omitted without greatly reducing the product, but here it is entirely left out. When oil of ants is purified the taste and smell are very pungent and aromatic, resembling oil of Cassia. It catches fire very readily and burns with a strong yellow flame. Its density is 1.1006 at 80.6° , (27° centig.); its boiling point 334.4 (168° centig.) It is pretty

soluble in water and more so in alcohol and ether. Potassium decomposes it with effervescence; but neither the aqueous nor the alcoholic solution of potash has any effect upon it.*

COMPOUNDS OF FORMYL WITH CHLORINE, BROMINE AND IODINE.

Protochloride of formyl, $C_2HCl=FOCl$.—One of the substances which Regnault obtained by the action of chlorine upon chloride of acetyl, namely $C_4H_2Cl_2$, is considered by Liebig as protochloride of formyl, its atomic weight being divided by two.

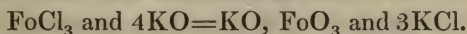
Bichloride of formyl, $C_2HCl_2=FOCl_2$; one of the substances formed by the action of chlorine upon chloride of ethyl, namely $C_4H_2Cl_4$, is so considered by Liebig, its atomic weight being divided by two.

Perchloride of formyl, chloroform, $C_2HCl_3=FOCl_3$. This compound is formed in various circumstances. It may be prepared by exposing a mixture of chloride of methyl (C_2H_3Cl) and gaseous chlorine to the direct rays of the sun; by distilling chloral with barytes-water or milk of lime but most conveniently by distilling a dilute solution of chloride of lime with acetone, alcohol or wood spirit. For this purpose 1 part of hydrate of lime is suspended in 24 parts of water, a current of chlorine sent through it till the greater part of the lime is dissolved, and a little milk of lime added to make the liquid alkaline. When the solution of chloride of lime has become clear by repose, $\frac{1}{4}$ th of its volume of alcohol is added, and after being left to itself for twenty four hours, the liquid is distilled by a gentle heat in a capacious retort. The product has an ethereal odour, and contains perchloride of formyl mixed with alcohol, on shaking it with water the perchloride separates as a dense liquid, and may be obtained perfectly pure by digesting it upon chloride of calcium, and distilling it again with concentrated sulphuric acid. (Liebig's *Traité*).

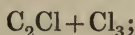
Perchloride of formyl is a colourless oily liquid, of an agreeable ethereal odour and sweetish taste; its density is 1.480 at 64.4° (18° centig.); its boiling point 141.44° (60.8° cent.) It

* Dr. Stenhouse, *Phil. Mag.*, 3rd Series, vol. 18, p. 122.

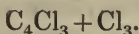
is inflamed with great difficulty but burns in the flame of a candle colouring it green. The alcoholic solution of potash destroys it, converting it into formiate of potash (Dumas), a property which the name chloroform refers to :



The density of its vapour is by experiment 4200, by calculation 4116: its combining measure 4 volumes. Chloroform may be distilled from sulphuric acid, potassium or potash without being sensibly altered. Exposed with chlorine to the direct rays of the sun it is decomposed and converted into hydrochloric acid and a particular *chloride of carbon* C_2Cl_4 , which boils at 172.4° (78° centig.), and of which the density of the vapour is 5300, and combining measure 4 volumes (Regnault). This chloride of carbon has been looked upon as a formic acid in which both the hydrogen and oxygen are replaced by chlorine :



while the well known sesquichloride of carbon is related in the same way to acetic acid :



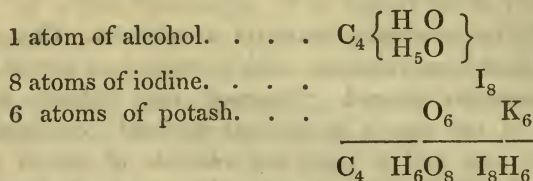
When the former chloride of carbon is made to pass in vapour through a porcelain tube at a dull red heat, it is divided into two new chlorides of carbon, of which the composition is expressed according to M. Regnault, by CCl and CCl_3 .

Chlorhydrate of chloride of formyl, $2\text{C}_2\text{HCl}$, HCl ; one of the products of the action of chlorine upon the chlorhydrate of the chloride of acetyl.

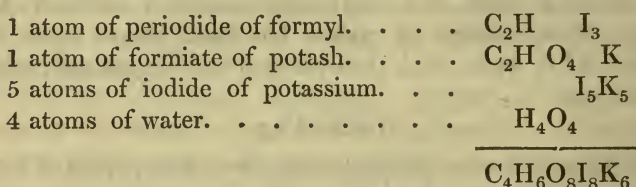
Perbromide of formyl, bromoform, $\text{C}_2\text{HBr}_3=\text{FoBr}_3$; prepared like the perchloride, and very analogous to it in properties; its density is 2.10. It is less volatile than the perchloride, and more easily decomposed by alkalies.

Periodide of formyl, iodoform, $\text{C}_2\text{HI}_3=\text{FoI}_3$.—This is a yellow volatile substance discovered by Serullas, which is often described as an iodide of carbon. It is obtained on adding an alcoholic solution of potash to a solution of iodine in alcohol, till the last is discoloured, carefully avoiding any excess of alkali. The alcohol is then expelled by gentle evaporation, and the iodide of formyl is deposited in crystals, which are purified from iodide of potassium by washing with pure water. This

compound is formed in consequence of the decomposition of 1 atom of alcohol and 6 atoms of potash, by 8 atoms of iodine, by which 1 atom of periodide of formyl, 1 atom of formiate of potash, 5 atoms of iodide of potassium and 4 atoms of water are produced (Liebig).



Equivalent to :



Iodoform crystallizes in brilliant yellow plates, and has a characteristic odour suggesting that of saffron. It is insoluble in water, but very soluble in alcohol, ether and wood spirit. It sublimes at 212° ; at 248° it undergoes decomposition and is resolved into carbon, iodine and hydriodic acid. It gives a peculiar liquid of a deep red colour and density 1.96, when distilled with chloride of phosphorus or with corrosive sublimate; this liquid contains chlorine, iodine and formyl.

Sulphuret of formyl, FeS_3 ? (Bouchardat). A liquid obtained by distilling 1 part of iodide of formyl with 3 parts of sulphuret of mercury; hydrate of potash converts it into sulphuret of potassium and formiate of potash.

Action of chlorine upon oxide of methyl.—Chlorine gas decomposes the oxide of methyl gas, forming hydrochloric acid and the following products, as observed by M. Regnault :

	Density.	Boiling point.	Density of vapour.
Oxide of methyl.	$C_2 H_3 O$		1570=2 v.
Monochlorinated oxide of methyl.	$C_2 H_2 Cl O$	1.315 105° cent.	4047=2 v.
Bichlorinated oxide of methyl.	$C_2 H Cl_2 O$	1.606 130° „	6367=2 v.
Perchlorinated oxide of methyl.	$C_2 Cl_3 O$	1.594 212° „	4670=4 v.

The combining measure of perchlorinated oxide of methyl differs, it will be observed, from the other members of the series. (*Annales de Chimie*, etc. lxxi. 353).

Chlorine is absorbed with great avidity by hydrate of oxide of methyl and a heavy oil formed, which has not yet been fully examined.

Action of chlorine upon chloride of methyl.—This also gives rise to a series of compounds, in which the proportion of chlorine increases as the action is prolonged. (Regnault).

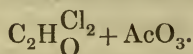
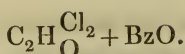
	Density.	Boiling point.	Density of vapour.
Chloride of methyl. C_2H_3Cl			1738=4 v.
Monochlorinated ditto. $C_2H_2Cl_2$	1.344	30.5° cent.	3012=4 v.
Bichlorinated do. (chloroform). C_2HCl_3	1.491	60.8° „	4230=4 v.
Perchlorinated ditto. C_2Cl_4	1.599	78° „	5245=4 v.

The monochlorinated chloride of methyl has an odour which is very sharp and is similar to that of Dutch liquid; treated with an alcoholic solution of potash, the former liquid gives only a very trifling precipitate of chloride of potassium, and distils over almost entirely without change.

The perchloride of carbon, C_2Cl_4 , which is named above perchlorinated chloride of methyl, is not altered by a solution of hydrosulphuret of the sulphuret of potassium. It is decomposed by heat and gives different chlorides of carbon according to the temperature.

At a dull red heat, this chloride C_2Cl_4 appears to be converted into another chloride of carbon C_2Cl_3 , supposing the combining measure of the latter to be 4 volumes, its density being 4082. This new chloride of carbon will therefore be isomeric with Faraday's sesquichloride C_4Cl_6 , but of only half the density. When decomposed at a higher temperature it gives small silky crystals of the chloride of carbon of Julin CCl . Lastly at a bright red heat the liquid chloride of carbon C_4Cl_4 is the principal product.

Chlorine acts readily upon the sulphuret of methyl and upon the compounds of oxide of methyl with acids or the compound methylic ethers. A benzoate and acetate of an oxichloride of formyl have been produced, having the following formulæ, (Malaguti):



A mixture of iodine, nitric acid and wood spirit left to itself for a long time, deposits yellow crystals. Bromine in the same circumstances gives a heavy oily liquid (Aimé).

SECTION III.

PRODUCTS OF THE DISTILLATION OF WOOD HAVING SOME RELATION TO OXIDE OF METHYL.

Xylite, lignone (Gmelin), a liquid which exists in commercial pyroxylic spirit, and is separated from the hydrate of oxide of methyl by distillation from chloride of calcium at 212° . MM. Weidmann and Schweizer, in their last memoir on these products, assign to xylite the formula $\text{C}_6\text{H}_6\text{O}_{2\frac{1}{2}}$. The density of its vapour was by experiment 2177, by theory 2159; its boiling point 142.7° (61.5° centig.); density 0.816. Pure xylite has an agreeable, sharp odour, and empyreumatic taste. It is miscible with water, dissolves but little chloride of calcium, and burns with a white flame.

Mesiten, $\text{C}_6\text{H}_6\text{O}_3$ (Weidmann and Schweizer), a liquid obtained by distilling equal parts of sulphuric acid and xylite, in which chloride of calcium is wholly insoluble. Its density is 0.808; boiling point 145.4° (63° centig.)

Xylitic acid, $\text{C}_4\text{H}_3\text{O}_{1\frac{1}{2}}$ (W. and S.), obtained by treating anhydrous xylite with hydrate of potash. The salt thus formed is supposed to be a compound of xylitate of potash with xylite, $3(\text{KO}, \text{C}_4\text{H}_3\text{O}_{1\frac{1}{2}}) + \text{C}_6\text{H}_6\text{O}_{2\frac{1}{2}}$. It is readily soluble in wood-spirit, but is insoluble in anhydrous xylite. Xylite oil and xylite resin are two other substances contained in an oil, formed, among other products, by the action of an excess of hydrate of potash upon xylite.

Mesite, $\text{C}_6\text{H}_6\text{O}_2$ (W. and S.). This liquid which, in its physical properties, very much resembles mesiten, exists in crude pyroxylic spirit, and comes over late in its rectification. Mesite may, therefore, be separated, by distillation with water, from xylite, as the latter passes over early. Mesite is also formed by

the action of potash and potassium upon xylite. It is colourless, volatile, and of an ethereal odour, boils somewhat above 158° , and is soluble in water.

Xylite naphtha, $C_6H_6O_{1\frac{1}{2}}$.—By the action of hydrate of potash upon mesite, acetic acid is formed and xylite naphtha. When pure, this liquid is colourless and very fluid, having an odour resembling oil of peppermint, but slightly soluble in water, soluble easily in alcohol, wood-spirit, xylite and ether. It boils at 230° , and burns with a white and smoky flame.

The principal products of the treatment of xylite-naphtha by an excess of hydrate of potash or potassium are xylite-oil and xylite-resin.

Xylite-resin, $C_{24}H_{18}O_3$; when pure, is a reddish, brown, brittle mass, fusible under 212° , but decomposed by a higher temperature. It is insoluble in water, or in solution of potash, and gives no precipitate with an alcoholic solution of acetate of lead. It is readily dissolved by alcohol, wood-spirit, xylite and ether.

Xylite-oil, $C_{12}H_9O_1$. To obtain this oil pure, it is necessary to act upon xylite with a great excess of hydrate of potash. It is colourless, but usually yellow, lighter than water and nearly insoluble in it, readily dissolved by alcohol, etc. It has a bitter, burning taste, a peculiar odour, boils considerably above 392° (200° centig.), and may be distilled without decomposition. It burns with a white, very smoky flame. When decomposed by hydrate of potash, xylite-oil gives acetic acid and a peculiar resin, $C_{48}H_{36}O_3$; not so fusible as xylite-resin.

When 1 part of anhydrous acetone is gradually mixed with 2 parts of hydrate of potash, well pulverised, the vessel being kept cool, and the mass mixed after six or eight days with water, a brown oily liquid separates; this may be washed with water to free it from undecomposed acetone, and distilled with water to separate it from a resinous body. This oil has the same boiling point and composition as xylite-oil, and appears to be identical with it. The resin has also the same composition as xylite-resin.*

Methol, $C_{12}H_9$; a liquid produced by the distillation of xylite with sulphuric acid; pure wood-spirit does not yield it, although it was first obtained by the treatment of the crude spirit; it is

* Læwig and Weidmann; Poggendorff's Annalen, 1, 299.

a hydrocarbon, and contains no oxygen. It does not mix with sulphuric acid, but by long digestion and agitation, it disappears entirely, and is partly converted into a black *resin*, $C_{24}H_{16}O$, which is insoluble in alcohol and wood-spirit, but soluble in ether and xylite. Methol is not converted into this resin by the action of air. The acid solution neutralised with carbonate of lime gives a white crystalline salt, containing *methol-sulphuric acid*, of which the formula when free is $HO,SO_3 + C_{12}H_9, SO_3$, or perhaps rather $HO, C_{12}H_8S_2O_5 + HO$.*

Mr. Scanlan has shown that crude wood-spirit contains free *aldehyde*, which he has extracted from it in a state of purity by submitting the crude spirit to successive distillations. L. Gmelin obtained *acetone* from the wood-spirit of the French manufactories; it distilled over first when the crude spirit was rectified from chloride of calcium.

Pyroxanthin, *eblanin*,† $C_{21}H_9O_4$ (Gregory and Apjohn); a crystalline substance of an orange colour, obtained by Mr. Scanlan on distilling crude pyroxylic spirit from slaked lime. It remains with the lime, and after neutralising the latter with acetic acid, may be taken up by alcohol, from which it is deposited in long needles or prisms having the colour of carbazotate of potash. It is insoluble in water and in alkalies, but soluble in alcohol, ether and concentrated acetic acid. It sublimes at 273° , but does not melt till it is raised to the temperature of 291° . Concentrated sulphuric acid dissolves it, and assumes a red blue colour.‡

SECTION IV.

OTHER PRODUCTS OF THE DISTILLATION OF WOOD, CONTAINED IN TAR.

Paraffin is a particular hydrocarbon, produced in the distillation of wood, and in many other circumstances, which has the same composition per cent as olefiant gas, or CH . It is a crys-

* F. Weidmann and E. Schweizer; Poggendorff's Annalen, xliii, 593; xlix, 135 and 293; 1, 265.

† From Eblana, Dublin.

‡ Liebig's Annalen for 1837; or Dr. Thomson's Organic Chemistry, Vegetables, p. 750.

talline substance, transparent and colourless, soft and not unlike stearic acid, inodorous and tasteless, fusible at 110.6° (43.75° centig.), and capable of being distilled at a higher temperature without alteration. A cotton-wick which has imbibed melted paraffin, burns without smoke or odour, like a wax taper. Its density is 0.870.

In a chemical point of view, paraffin is distinguished for a remarkable indifference to other bodies; hence the name paraffin (*parum affinis*) assigned to it by M. Reichenbach, its discoverer. It is not decomposed by chlorine, by alkalies or acids. Paraffin is very soluble in ether and oil of turpentine; boiling alcohol dissolves only 3.45 per cent of its weight. This and the other principles existing in tar are obtained by long and intricate processes, which cannot be shortly described.*

Eupion, C_5H_6 , is best obtained from animal tar. It is a colourless, very limpid liquid (whence its name), without odour or taste, of density 0.655, not frozen by -4° , boiling at 336.2° (169° centig.), and distilling over without change. It burns easily by means of a wick, with a bright flame and no smoke. Eupion is insoluble in water, but soluble in alcohol. It is not altered by potassium, by chlorine or iodine, which it dissolves, nor by acids or alkalies.—(Reichenbach, *Ann. de Chim.* l, 69.)

Creosote, $C_7H_{42}O$ (Ettling), is present in wood-smoke, in tar, and generally in wood-vinegar (pyroligneous acid), to which it communicates its odour, taste and antiseptic properties. It is an oily colourless liquid, of high refracting power, of which the odour is penetrating and disagreeable, analogous to that of smoked meat, and the taste burning and very caustic. Its density is 1.037 at 68° ; it boils at 397.4° (203° centig.), and is not frozen by a cold of -16.6° (-27° centig.). It burns with a very smoky flame.

Creosote forms two different compounds with water at the ordinary temperature; one is a solution of 1.25 parts of creosote in 100 parts of water; the other, on the contrary, a solution 10 parts of water in 100 of creosote. Acetic acid appears to be a special solvent of creosote; these two liquids mix in all proportions. Potassium is decomposed in it with effervescence and formation of potash. Creosote forms in the cold two com-

* Reichenbach; *Ann. de Chimie*, etc. t. 30, p. 69. Also Dr. Thomson's *Organic Chemistry, Vegetables*, p. 723; or *Traité de Chimie*, par M. Dumas, t. v. p. 652.

pounds with potash ; one is anhydrous, liquid, of an oily consistence, the other hydrated and crystallized in white pearly plates ; they are both decomposed by all acids, even carbonic acid. It mixes in all proportions with alcohol, ether, sulphuret of carbon, oil of petroleum and acetic ether. Creosote is remarkable for dissolving a large number of organic colouring matters, including cochineal, dragon's blood, litmus, madder, saffron, and even indigo, when heated. It coagulates albumen, a property upon which its corrosive action upon animal tissues may depend. Butcher-meat or fish dipt in it, and then exposed to air, does not putrify,* but acquires the agreeable flavour of the same kind of food when well smoked.

Picamar (in *pice amarum*) is a transparent and nearly colourless liquid, of the consistence of an oil somewhat thickened ; its odour is weak and peculiar, its taste insupportably bitter and burning, then cooling, like that of peppermint. Its density is 1.10 at 68° ; its boiling point 518°. It is the bitter principle, according to M. Reichenbach, of all empyreumatic products. It forms crystalline compounds with the alkalies and alkaline earths, in which the latter are not neutralised. It is insoluble in water, but soluble in alcohol and ether.

Pittacal, a beautiful colouring matter, discovered by Reichenbach in the oil of tar ; the latter substance, when free from acid, assuming a beautiful blue on the addition of barytes-water to it. This substance when precipitated or obtained by evaporation forms a deep blue mass, solid and friable, like indigo. It assumes also a coppery lustre, like indigo, when rubbed. It is inodorous, insipid and not volatile. Pittacal is insoluble in water, but is suspended in that liquid in a state of such minute division as to pass through a paper filter, and colour the liquid blue. Its solution in acetic acid is of a rose red colour, and recovers a very fine blue colour on the addition of an excess of alkali. M. Reichenbach recommends it as a re-agent even more sensible than litmus to the action of acids and alkalies. It is not soluble in alcohol, ether or eupion. It is not altered by air and light.

Pittacal gives precipitates of a fine violet blue colour, with acetate of lead, chloride of tin, ammoniacal sulphate of copper and acetate of alumina. This substance may be available ulti-

* Hence the name creosote, from κρεας flesh, and σοξω I save.

mately, in the opinion of M. Reichenbach, as a colour in dyeing.

Besides the bodies described, other substances have been found among the products of the distillation of wood, to which the names *cedrinet*, *chrysene*, *pyrene* and *capnomor* have been given.

PRODUCTS OF THE DISTILLATION OF COAL.

The general products of the distillation of coal, which appear in gas-making, are: 1, the residuary carbon or coke; 2, gaseous compounds of carbon and hydrogen, including olefiant gas (page 422); 3, a watery liquid, containing salts of ammonia; and, 4, tar.

When the tar is distilled with water, an oily liquid comes over, and there remains behind a black resinous substance, or pitch, of the nature of which little is known. The oil is a mixture of several bodies, some of which are capable of combining with bases, and some with acids. Particular substances have been isolated, to which the names, *leucol*, *pyrrol*, *cyanol*, *carbolic acid*, *rosolic* and *brunolic acids* are applied, but the most remarkable product in coal-tar is *naphthaline*, which is sometimes found sublimed pure, in white crystalline plates, in the gas apparatus.

NAPHTHALINE.

Formula: $C_{20}H_8$. M. Laurent has observed that this substance is best obtained from tar which is somewhat old. The tar is boiled in air till it is deprived of water, and then distilled in a retort with a copper adapter or connecting tube, and glass receiver. The first portion of oil distilled is of a yellowish colour, which becomes dark coloured in air, and allows much naphthaline to fall when cooled to 14° or 10° Fahr. If re-distilled, and the last portions received apart, they yield naphthaline in large quantity when cooled. To purify naphthaline, it is crystallized twice from alcohol, taking care to press the crystals each time in folds of cotton cloth. If the oil is submitted for some time to a current of chlorine, it yields afterwards an increased product of naphthaline.

Naphtaline is in transparent and colourless plates, has a strong peculiar and not unpleasant odour, a burning aromatic taste, is denser than water, insoluble in it, melts at 176° , boils at 422.6° (217° centig.), and condenses in shining leaflets. The density of its vapour is 4528 by experiment, and 4488 by calculation; its combining measure is 4 volumes. Naphtaline burns, when heated, with a white smoky flame. It is very soluble in alcohol and ether, and crystallizes from these solutions on dilution with water. Naphtaline is peculiarly the product of a high temperature, and is furnished by alcohol and organic matters in general when heated to redness.

Naphtaline dissolves in concentrated sulphuric acid, upon the application of heat; with anhydrous sulphuric acid it combines when heated, and forms a fine purple red liquid. The compound contains three peculiar acids, which on diluting the mass with water and neutralising it with carbonate of barytes, are obtained in three different barytes salts, which may be separated and distinguished from each other by their unequal solubility and different crystallization. They are:

Naphtalin-hyposulphuric acid or *sulphonaphtalic acid*, $\text{HO} + \text{C}_{20}\text{H}_8\text{S}_2\text{O}_5$. It is soluble in water and crystallizes, is sour and bitter, with a metallic after-taste. The hyposulphuric acid it contains is not neutralised by the naphtaline, and combines with the usual proportion of base to form a neutral salt. *Sulphonaphtalate of barytes* $\text{BaO} + \text{C}_{20}\text{H}_8\text{S}_2\text{O}_5$, crystallizes in brilliant light spangles, burns in the flame of a candle, is insoluble in alcohol. It parts with an atom of water when heated; its formula may then be $\text{BaO} + \text{C}_{20}\text{H}_7\text{S}_2\text{O}_4$.

Naphtin-hyposulphuric acid or *sulphonaphtic acid*, $\text{HO} + \text{C}_{11}\text{H}_{44}\text{O}_2\text{S}_2\text{O}_5$, is not crystallizable, and very soluble in water.

Glutinhypsulphuric acid is separated from its salts by hydrochloric acid as a milky substance, which falls and collects together in transparent, clammy drops; its salts do not crystallize.

When naphtaline is dissolved in excess by sulphuric acid, and water added, the excess is precipitated, but in an altered state, for when the precipitated naphtaline is distilled with water, it leaves behind a fatty matter, from which alcohol separates two

new compounds, *sulphonaphthaline*, $C_{20}H_8, SO_2$ and *sulphonaphthalide*, $C_{24}H_{10}, SO_2$. Both are inodorous and insoluble in water.

By the action of chlorine upon naphthaline, two compounds of that substance with chlorine in different proportions are formed; and by the abstraction of hydrochloric acid from these, or continued action of chlorine, several other compounds are produced:

1. $C_{20}H_8Cl_2 = C_{20}H_7Cl + HCl$
2. $C_{20}H_8Cl_4 = C_{20}H_6Cl_2 + H_2Cl_2$
3. $C_{20}H_6Cl_2 = C_{20}H_5Cl$
4. $C_{20}H_6Cl_6 = C_{20}H_4Cl_4 + H_2Cl_2$
5. $C_{20}H_5Cl_3 = C_{20}H_4Cl_2$

The first of these compounds *chlorhydrate of chloro-naphthalase* of Laurent is formed when naphthaline absorbs chlorine gas at the usual temperature; it is a yellow oil, denser than water and insoluble in it. When treated with potash it loses HCl , and gives the *chloronaphthalase* of Laurent, $C_{20}H_7Cl$.

The second, *chlorhydrate of chloronaphthalase* of Laurent, when naphthaline is saturated with chlorine gas at 140° . It crystallizes from ether in transparent rhomboidal tables, requires a temperature of 320° to fuse it, and forms a crystalline mass on cooling.

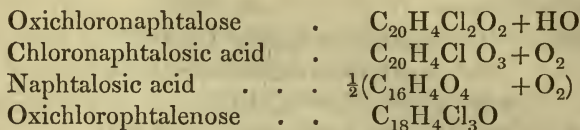
The third, *chloronaphthalase* of Laurent, is produced by the distillation of the second, or by treating it with an alcoholic solution of potash, with the separation of 2 atoms of hydrochloric acid. It crystallizes from alcohol in rhombic prisms, is tasteless and inodorous, and fuses at 111.2° (44° centig.). Two other isomeric compounds of the same formula exist, one an oil, the other obtained by potash.

The fourth compound, *chlorhydrate of chloronaphthalose* of Laurent, is produced by the action of chlorine gas upon the third, at the usual temperature. It much resembles the body from which it is derived, fuses at 105.8° (41° centig.), and may be sublimed without change.

The fifth compound, *chloronaphthalise* of Laurent, is the product of the action of chlorine on the first or fluid chloride of naphthaline in sunshine, or with heat and subsequent distilla-

tion of the oil formed. It crystallizes from ether in large striated prisms, which are colourless, inodorous, soft like bees'-wax, fusible at $163^{\circ}.4$ (73° centig.). This compound is a naphthaline in which 3 atoms of hydrogen are replaced by 3 atoms of chlorine. (Laurent, Ann. de Chim. &c. lxi, 196).

M. Laurent has obtained two neutral substances and two acids, from the action of nitric acid upon the naphthalic chlorides (Ann. de Chim. lxxiv, 26) :



Nitronaphtalide (*nitronaphtalase*), $C_{20}H_7 + NO_4$, is produced on heating naphthaline with nitric acid, by the separation of HO. It crystallizes from alcohol in four-sided prisms, of a sulphur-yellow colour, fuses at $109^{\circ}.4$ (43° centig.), and may be sublimed when cautiously heated ; when suddenly heated it burns.

Nitronaphtdehyde (*nitronaphtalese*), $C_{20}H_6 + 2NO_4$, is formed by boiling the former compound, or naphthaline and nitric acid till no oily body floats on the surface of the liquid. It falls upon the cooling of the liquid as a yellow crystalline powder, fusible at 365° , which may be sublimed without change, and is insoluble in water and alcohol. (Laurent).

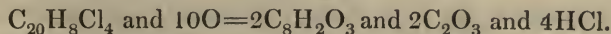
The action of nitric acid on naphthaline being continued for a longer time and at a high temperature, after the expulsion of the nitric acid in nitrous fumes and the sublimation of the naphtalese, a feeble explosion takes place, and a coaly mass remains in the retort. By repeating the treatment of this mass with nitric acid, M. C. de Marignac obtained the three following new products: 1, *Nitronaphtalise*, $C_{20}H_{10}N_3O_{12}$ or $C_{20}H_{10} + 3NO_4$; a yellow, glutinous, resinous substance, insoluble in water, dissolved out of the mass by ether. This substance is named by Marignac according to the plan followed by Laurent of distinguishing compounds obtained successively from the same root by the vowels, *a, e, i, o*, etc.; the two preceding compounds being nitronaphtalase and nitronaphtalese, this falls to be named nitronaphtalise. Alkalies decompose this substance, and convert it into—2, a *brown matter*, $C_{12}H_3NO_5$, carbonic acid and ammonia; 3, *nitronaphtalic acid*, $2HO + C_{16}H_5NO_{12}$; a bibasic

acid, soluble in water, forming crystallizable salts. The salt of *ammonia* is white, with the lustre of mother of pearl, and resembles the crystalline plates of naphthaline; it is readily dissolved by water, and pretty soluble in alcohol. The salts of *silver* and *barytes* contain two atoms of metallic oxide, the salt of *lead* four atoms.

M. de Marignac also obtained a *volatile liquid*, which distilled over with the excess of nitric acid, in treating the hydrochlorate of chloronaphtalese ($C_{20}H_8Cl_4$) with that acid, of which the constitution is remarkably simple, $C Cl NO_4$, or $C Cl + NO_4$. This liquid, which is not named, is perfectly colourless, transparent, of density 1.685 at 59° , of an odour excessively irritating, like that of chloride of cyanogen, and affecting the eyes, neutral to test-paper. Water dissolves a mere trace of it, but acquires thereby its smell and taste. It dissolves easily in alcohol and ether; nitric and hydrochloric acids dissolve only a very little of it. Its boiling point appears to be not greatly above 212° . The aqueous solution of potash has no action upon it, the alcoholic solution dissolves it easily, and after a time, a crystalline potash-salt falls, which is decomposed when heated, with explosion. The density of its vapour was not ascertained.

The *naphthalic acid*, which is formed and remains in the retort in the preceding process, did not possess the properties or composition of the acid which M. Laurent obtained by a similar process. Marignac's naphthalic acid contains nitrogen, with carbon and hydrogen in the proportion of C_8H_5 , which is inconsistent with the formula of the following acid.*

Naphtalic acid, $HO + C_8H_2O_3$, is formed on heating with nitric acid the second compound or solid chloride of naphthaline in the foregoing list (the chlorhydrate of chloronaphtalese); ruddy fumes are given off, and the acid solution gives on concentration a white crystalline crust, which is naphthalic acid. One equivalent of chlorhydrate of chloronaphtalese and 10 equivalents of oxygen give 2 equivalents of naphthalic acid, 2 equivalents of oxalic acid, and 4 of hydrochloric acid :



* C. de Marignac, in Liebig's Annalen, vol. 38, pp. 1 & 13.

It crystallizes by sublimation in long thin prisms, resembling benzoic acid, which are inodorous, have a weak taste, fuse at 221° , are soluble with difficulty in water, have an acid re-action and form salts with bases. (Laurent.)

Paranaphtaline, $C_{30}H_{12}$; accompanies naphthaline in tar, and is deposited by the distilled oil when greatly cooled in crystalline grains. It is distinguished from naphthaline by its sparing solubility in boiling alcohol. It is also less fusible and less volatile, fusing at 356° and boiling above 572° (300° centig.). Its best solvent is oil of turpentine. It contains carbon and hydrogen in the same proportion as naphthaline, but on taking the density of its vapour, it is found that 3 volumes of naphthaline represent only 2 of paranaphtaline; the density of the latter is 6732. (Dumas and Laurent, Ann. de Chim. 1, 187).

SECTION V.

BITUMEN.

A tarry matter, known as bitumen, is found native in various parts of the world, sometimes so consistent as to be termed pitch or asphalt, and often liquid and thin, as the native petroleum or naphtha of Persia and Rangoon. The latter, however, always holds much fixed matter in solution.

According to the recent observations of MM. Pelletier and Walter, natural naphtha consists of several liquid and one solid compound, paraffin namely, which it contains ready formed. The liquid compounds are hydrocarbons, which these chemists name naphtha, naphtene and naphtol. They are separated from each other by distillation, as they have different boiling points.

Naphtha, $C_{14}H_{13}$; boils between 185° and 194° , is decomposed by sulphuric and nitric acid, particularly with the aid of heat, less affected by chlorine; iodine dissolves in it. The density of its vapour is by observation 3400, by calculation 3390.

Naphthene, $C_{16}H_{16}$; is denser than naphtha, oily, and boils at 239° . The density of its vapour is by observation 4000, by calculation 3920. Naphtene thus forms, from its composition,

the fourth member of the series of hydrocarbons to which olefiant gas belongs :

Methylene (hypothetical)	C_2	H_2
Olefiant gas	C_4	H_4
Oil gas	C_8	H_8
Naphtene	C_{16}	H_{16}
Cetene	C_{32}	H_{32}

Naphtol, $C_{24}H_{22}$; like naphtene, greatly resembles naphtha in its chemical properties, boils at 374° . The density of its vapour is by observation 5300, by calculation 5600. Naphtol and naphtene give compounds with chlorine, bromine and iodine.

It is evident from its composition that natural naphtha must be the product of the action upon vegetable matter of a high temperature, which has not however exceeded a red heat.*

CHAPTER IV.

AMYGDALIN AND THE BODIES DERIVED FROM ITS DECOMPOSITION.

SECTION I.

AMYGDALIN.

The formula of anhydrous amygdalin is $C_{40}H_{27}N O_{22}$.

This is a principle in the bitter almond and berries of the cherry-laurel, of which the discovery is due to Robiquet and Boutron-Charlard. Its singular decomposition and the nature and relations of the products resulting from it were ably investigated by MM. Liebig and Wœhler in a memoir, the publication of which formed an important era in the progress of organic chemistry (An. de Chim. li, 273.)

A fat oil is obtained by submitting blanched bitter almonds to great pressure between two hot iron plates; the matter which remains, or the almond cake, is the source of amygdalin. It is treated with boiling alcohol of 93 or 94 per cent applied to it in successive portions, and the alcoholic solutions evaporated by a water-bath to a syrupy consistence. To remove a quan-

* Journal de Pharmacie, t. 26, p. 549.

tity of sugar which prevents the amygdalin from crystallizing, the residue is diluted with water, a little yeast added to it, and it is left to ferment in a warm place. After the fermentation ceases, the liquid is filtered and evaporated again by a water-bath to a syrupy consistence. On mixing the syrup with a portion of strong alcohol of 94 per cent, all the amygdalin precipitates in the form of a white crystalline powder, which is pressed in folds of filter paper, and afterwards purified by new crystallizations from alcohol. (Liebig).

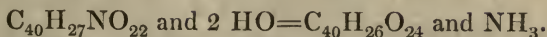
As crystallized from alcohol, amygdalin retains a portion of that substance in combination, which it loses when exposed to air. At the ordinary temperature it is scarcely soluble in anhydrous alcohol, but is more easily dissolved by boiling alcohol. It is very soluble in water, and crystallizes from a solution saturated at 104° in large transparent prisms, of a silky lustre which contain 10.57 per cent of water, or 6 atoms; dried in vacuo over sulphuric acid the crystals lose 3.52 per cent of water, equivalent to 2 atoms. The crystals are not volatile, but are decomposed by a high temperature, diffusing the odour of hawthorn, and leaving a bulky charcoal.

Dry chlorine has no effect upon amygdalin; humid chlorine converts it into a bulky white powder, insoluble in water and alcohol, which has not been examined. Heated with dilute nitric acid, or with peroxide of manganese and dilute sulphuric acid, amygdalin produces ammonia, volatile oil of bitter almonds, benzoic acid, formic and carbonic acids. Hypermanganate of potash in decomposing amygdalin gives rise to cyanate and benzoate of potash. Caustic alkalies convert amygdalin into ammonia, which is disengaged, and amygdalic acid, a peculiar acid, which remains in combination with the alkali.

AMYGDALIC ACID.

Formula: $\text{HO} + \text{C}_{40}\text{H}_{26}\text{O}_{24}$. This acid was first obtained by Liebig and Wöehler, by the action of alkalies upon amygdalin. It is best prepared by dissolving amygdalin in barytes-water, and maintaining the mixture in a state of ebullition, so long as ammonia is disengaged; the barytes is then removed by sulphuric acid, and the liquid evaporated by a water-bath. In the formation of this acid, 1 atom of amygdalin and 2 atoms of

water are resolved into 1 atom of ammonia and 1 atom of anhydrous amygdalic acid :



Amygdalic acid is obtained by evaporation as a transparent colourless amorphous mass ; it has a very agreeable acid taste, is insoluble in alcohol and ether, but so soluble in water as to deliquesce in damp air.

Nitric acid and the mixture of peroxide of manganese and dilute sulphuric acid act on amygdalic acid as on amygdalin, allowing for the absence of nitrogen from the former, the products being volatile oil of bitter almonds, formic and carbonic acids, all of which are disengaged in the state of gas.

Little is known of the amygdalates ; they appear to be in general soluble salts, with the exception of a basic salt of lead. Amygdalin, it will be observed, has the composition of amygdalate of oxide of ammonium, from which the elements of 3 atoms of water have been abstracted ; or it has lost 1 atom of water more than a true amygdalamide (Liebig).

SECTION II.

BENZOYL SERIES OF COMPOUNDS.

Benzoyl or *benzoïle*,* $\text{C}_{14}\text{H}_5\text{O}_2=\text{Bz}$. This is the hypothetical radical of a series of compounds, including benzoic acid, (from which it derives its name), and the essence or volatile oil of bitter almonds. The last substance is derived from amygdalin by various means. Amygdalin exists also in the kernels of many fruits, and in the leaves of the laurel.

BENZOIC ACID.

Formula: $\text{HO},\text{C}_{14}\text{H}_5\text{O}_3=\text{HO}, \text{BzO}$. This acid exists ready formed in several resins, particularly benzoin and dragon's blood. It is produced by the decomposition of amygdalin by oxidating matters, by the oxidation of essence of bitter almonds, of hippuric acid, and in many other circumstances.

* *Benzule* of several English chemical writers.

To prepare benzoic acid from the resin, Dr. Mohr directs 1 pound of it to be broken and spread uniformly in a cast iron bason, 8 or 9 inches in diameter and 2 inches deep, the mouth of which is then covered, like a drum, by unsized paper pasted down at the edges. A cylindrical vessel of paper of the size and ordinary form of a man's hat is pulled over this, and bound about the bason by a thread. The bason is then placed on a sand-bath for three or four hours, attention being paid to the management of the heat, for the beauty and purity of the product depend entirely upon the slowness and regularity with which the sublimation is effected. The paper cylinder is found completely filled with superb crystals of benzoic acid of splendid whiteness and perfectly free from the black empyreumatic oil which they are generally soiled with; but having on the contrary a strong and very agreeable odour of benzoin. This process yields about 4 per cent of benzoic acid.

Benzoic acid is also prepared in the humid way; the resin is finely pulverised and care taken to mix it intimately with an equal weight of hydrate of lime; the mixture is then boiled with twenty times its weight of water by which the benzoate of lime is dissolved; the solution is filtered, and after being concentrated to about one-fifth of its bulk hydrochloric acid is added, by which the benzoic acid is liberated, and crystallizes on cooling. The chief point to be attended to in this process is the mixing of the resin and hydrate of lime, which must be intimate, otherwise the mass agglomerates in boiling water, and the benzoic acid can only be obtained by reducing the mass to powder and mixing it again with hydrate of lime.

The benzoic acid may be purified by a second sublimation, or by sending a stream of chlorine through its solution in boiling water (Liebig's *Traité*.)

Benzoic acid crystallizes when sublimed in long hexagonal silky needles; when pure it is colourless and inodorous; but it acquires by heat an odour, analogous to that of benzoin. Its taste is sweet and hot, but quite peculiar. It reddens litmus feebly; water dissolves $\frac{1}{17}$ of its weight of benzoic acid at 212° , and $\frac{1}{200}$ only at the ordinary temperature. It is soluble in two parts of alcohol and the same quantity of ether, and dissolves also in oil of turpentine. Benzoic acid fuses at 248° , and sublimes at 293° , phosphorescing in the dark; it boils at $462^{\circ}.2$ (239°

centig.) ; the density of its vapour is 4270 by experiment, and 4260 by calculation. Heated in open air it allows a white vapour to diffuse, which greatly irritates the fauces and provokes coughing. It is very inflammable, and burns with a white smoky flame without leaving any residue.

Benzoates. Benzoic acid is readily dissolved by alkalies and alkaline carbonates, and also by phosphate of soda. Several insoluble benzoates are dissolved, according to Lecanu and Serbat, by acetates of potash and soda and nitrate of soda, while they are insoluble, in nitrate and sulphate of potash, and sulphate of soda. *Ammonia* forms a neutral and acid benzoate ; the last presents itself in large regular crystals. The salts of *potash*, *soda*, *lithia*, and *magnesia* are very soluble, and crystallize with difficulty. The salt of *lime* is soluble in 20 parts of cold water, and in a greater proportion in boiling water ; it crystallizes in flexible needles, or brilliant prisms, which contain 1 atom of water of crystallization. Benzoate of *alumina* is obtained as a crystalline precipitate. Benzoates of *manganese* and *protoxide of iron* are pretty soluble. Neutral benzoate of *peroxide of iron*, $\text{Fe}_2\text{O}_3 + 3\text{BzO}$, is soluble in water and alcohol and crystallizable. But peroxide of iron is thrown down in the form an insoluble sub-benzoate, of a reddish white or buff colour, when a soluble benzoate is added to a solution of peroxide of iron, previously neutralised without precipitating any peroxide of iron by means of ammonia. To prevent the decomposition of this precipitate and the formation of a soluble benzoate of iron, it should be washed by a solution of sal ammoniac. Benzoate of ammonia is often employed to separate peroxide of iron from oxides of manganese, nickel, and zinc, but when the solution contains at the same time alumina, yttria, zirconia, or glucina, the process does not answer, as the benzoates of these oxides are equally insoluble with that of peroxide of iron. Benzoate of *lead* is nearly insoluble in water, but soluble in acetic acid, from which it may be obtained crystallized in plates, which contain 2 atoms of water, one of which it abandons when dried at 212° . Solutions of an alkaline benzoate and trisacetate of lead, give a white anhydrous and insoluble precipitate, which is basic benzoate of lead consisting of 2 atoms of benzoic acid united with 3 atoms of oxide of lead. Benzoate of *silver* is obtained in colourless needles, flattened and brilliant, on treating

a boiling and dilute solution of an alkaline benzoate with nitrate of silver, and allowing the liquid to cool.

HYDRURET OF BENZOYL, OR ESSENCE (VOLATILE OIL) OF BITTER ALMONDS.

Formula $C_{14}H_5O_2 + H=Bz,H$. The crude oil obtained by distilling laurel leaves or bitter almonds with water, contains hydrocyanic acid, benzoic acid and some benzoine (a solid oil); it is purified by a new distillation with water, protochloride of iron and hydrate of lime in a thin liquid. The oil which distils over may be dried perfectly by digestion with chloride of calcium.

Pure hydruret of benzoyl is a transparent colourless liquid, of high refracting power; its odour is strong and peculiar having some resemblance to that of hydrocyanic acid, its taste burning. It is poisonous. The density of the oil is 1.043, its boiling point 356° ; its vapour may be transmitted through a tube heated to redness without being decomposed. It inflames easily in air, and burns with a white smoky flame. It is soluble in 30 parts of water, and may be mingled in all proportions with alcohol and ether. Nitric acid dissolves hydruret of benzoyl, but converts it with difficulty into benzoic acid. Hydruret of benzoyl is gradually converted in air into benzoic acid by absorbing 2 atoms of oxygen, an atom of water being formed at the same time which combines with the benzoic acid formed. In presence of an alkali it absorbs oxygen rapidly and is transformed almost immediately into a benzoate. When mixed with dry hydrate of potash, and distilled at a high temperature out of contact with air, it forms benzoate of potash, by the decomposition of water, and pure hydrogen gas is disengaged. Submitted to a moderate heat with an alkali it gradually produces, according to Fremy, an alkaline benzoate and a volatile oily liquid very rich in hydrogen. Dilute solutions of the alkalis, barytes, or lime-water, dissolve hydruret of benzoyl, but do not alter it, even when kept for 24 hours at 140° or 160° , provided air is excluded. But all these solutions furnish a notable quantity of the solid benzoine, when after having added to them some drops of hydrocyanic acid they are exposed to a temperature of 158° . On treating hydruret of benzoyl

with an alcoholic solution of potash, it passes in a few seconds into benzoate of potash which floats upon the alcohol; a portion of the hydruret of benzoyl which loses oxygen being converted at the same time into an oil of unknown composition retained in solution by the alcohol.

Chloride of benzoyl $C_{14}H_5O_2 + Cl = Bz,Cl$; is formed on transmitting chlorine gas through dry hydruret of benzoyl, so long as hydrochloric acid is disengaged, and heating the yellow liquid to expel the excess of chlorine, till it becomes colourless. The atom of hydrogen of the hydruret of benzoyl is removed by one atom of chlorine, and replaced by another, as in ordinary substitutions.

Chloride of benzoyl is a colourless liquid, of a very penetrating and disagreeable odour, which affects the eyes; its density is 1.106; it boils at 383° (195° centig.). It may be distilled from lime or barytes without change. It mixes with ether and bisulphuret of carbon without decomposition. Cold water converts it more slowly than hot water into hydrochloric and benzoic acids; with alkalis it produces an alkaline benzoate and chloride of the same metal. With alcohol it produces benzoate of ether and hydrochloric acid.

Bromide and iodide of benzoyl crystallize in transparent colourless plates.

Sulphuret of benzoyl is obtained by distilling chloride of benzoyl with sulphuret of lead, as a yellow oil, which fixes as a soft crystalline mass, having a peculiar disagreeable odour.

Cyanide of benzoyl is prepared by distilling chloride of benzoyl with cyanide of potassium; it is, after rectification, a colourless oil having a strong cinnamon odour which excites tears.

Benzamide, $Bz + NH_2 = Bz,Ad$; is prepared by saturating chloride of benzoyl by dry ammoniacal gas; pulverising the white solid mass which is formed, washing it with cold water to remove sal ammoniac, and dissolving the residue in boiling water, which deposits the benzamide on cooling. It crystallizes in right rhomboidal prisms, or in small tables of a pearly lustre, fuses at 239° into a colourless liquid, and may be distilled at a higher temperature. It is soluble in alcohol and ether, as well as in water. Acids and alkalis decompose it, with the presence of water, into ammonia and benzoic acid.

Formobenzoïlic acid, $\text{HO} + \text{BzH}_2\text{C}_2\text{HO}_3$. This acid contains hydruret of benzoyl in combination with formic acid. It is the result of the action of dilute hydrochloric acid upon the crude distilled water of bitter almonds which contains the essence and hydrocyanic acid. The latter acid is decomposed in contact with water and a strong acid, into ammonia and formic acid, the last of which unites in the nascent state with the oil. This acid is a white crystalline powder, very acid, fusible into an oily liquid by heat with loss of water, soluble easily in water, alcohol and ether; capable of decomposing with aid of heat the acetates, carbonates and benzoates. Its aqueous solution when submitted to oxidating agencies, such as chlorine, nitric acid, and peroxide of manganese with dilute sulphuric acid, gives carbonic acid and hydruret of benzoyl.

Formobenzoïlic acid has the same saturating power as formic acid, and belongs to that class of acids into the constitution of which some foreign body enters without neutralising them. In the formation of its salts, the basic water of the formula above is replaced by a metallic oxide.

Benzoate of hydruret of benzoyl; a body which consists of 1 atom of hydrated benzoic acid united with 2 atoms of hydruret of benzoyl. It is prepared by saturating the crude essence of bitter almonds by humid gaseous chlorine; after some time the new compound is deposited in a crystalline mass, which is washed with cold ether. It forms either a crystalline powder of great whiteness, or slender short prisms of a square base, transparent and brilliant. It is soluble in alcohol, very slightly soluble in cold ether, and insoluble in water. It is decomposed immediately by an alcoholic solution of hydrate of potash, which deposits benzoate of potash after a time in regular crystals.

HIPPURIC ACID.

Formula: $\text{HO} + \text{C}_{18}\text{H}_8\text{NO}_5$.

This acid was discovered by Liebig, and obviously belongs to the benzoyl series, although its exact place cannot at present be assigned to it with certainty. It has been viewed as a compound of benzamide with an organic acid namely C_4HO_3 (aconitic, fumaric or equisetetic acid); or as a compound of hydruret of benzoyl,

hydrocyanic and formic acids. It exists in large quantity in the urine of herbivorous mammals, and was first derived from that of the horse; hence its name.

To prepare it the fresh urine of the cow or horse is evaporated by a gentle heat, care being taken not to allow it to enter into ebullition; it is then made sharply acid by means of hydrochloric acid, and left to itself. The hippuric acid which crystallizes from this liquid is coloured and impure, but may be purified by adding a little hydrochloric acid to it with portions of chloride of lime till the odour and colour disappear.

Hippuric acid crystallizes in pretty large semi-transparent prisms of four sides and dihedral summits, which have a slightly bitter taste, and redden litmus strongly. They fuse by heat into an oily liquid without loss of weight; at a higher temperature the acid undergoes decomposition and is converted into benzoic acid and benzoate of ammonia, which distil over in red drops, diffusing an agreeable odour like that of the Tonquin bean, which is occasioned by an oily product of the reaction; while towards the end of the distillation hydrocyanic acid appears and a porous residue of charcoal. Cold water dissolves $\frac{1}{100}$ of hippuric acid, hot water dissolves it very abundantly; it is more soluble in alcohol, and very slightly soluble in ether.

Hydrochloric acid dissolves hippuric acid without decomposing it; nitric acid converts it almost immediately into benzoic acid. Peroxide of manganese and sulphuric acid convert it, with the aid of heat, into carbonic acid, ammonia and benzoic acid. Boiled with puce coloured oxide of lead, hippuric acid is converted into benzamide and carbonic acid.

After the urine of the horse is left to itself for a long time, or evaporated rapidly, it contains benzoic acid and no hippuric acid. M. Liebig expresses an opinion that hippuric acid is not a product of the animal economy, but comes from the food of the animals, in which it may exist ready formed. For it is observed that the urine of horses living on green food, always furnishes hippuric acid, while the urine of animals fed on dry herbs or hay, which has undergone a kind of fermentation, contains only benzoic acid. Mr. Alexander Ure has since made the curious observation that benzoic acid taken internally by man is discharged in the urine as hippuric acid, while the pro-

portion of uric acid in the urine suffers at the same time a great diminution or is reduced to nothing.*

The *hippurates* of the alkalies and alkaline earths are soluble and crystallizable. Those of the metals proper with the exception of iron are very sparingly soluble in cold, but more soluble in hot water and crystallize on cooling. The stronger acids separate hippuric acid from all the hippurates; distilled with lime or hydrate of potash they give ammonia with an oily liquid supposed to be benzin.

PRODUCTS OF THE DECOMPOSITION OF BENZOYL COMPOUNDS.

Hyposulphobenzoic acid, $2\text{HO} + \text{C}_{14}\text{H}_4\text{O}_3, \text{S}_2\text{O}_5$; a bibasic acid discovered by Mitscherlich. It is prepared by conducting the vapour of anhydrous sulphuric acid into a dry receiver containing benzoic acid and surrounded by cold water; a viscid mass is formed like turpentine, which is taken up by water, and after the uncombined benzoic acid has subsided from the liquid, the latter is neutralised with carbonate of barytes, and after evaporating the mixture, some hydrochloric acid is added to it; the acid hyposulphobenzoate of barytes crystallizes upon cooling. The free acid is obtained by precipitating the barytes of the last salt by sulphuric acid, filtering, evaporating the solution by the naked fire and finally in vacuo over sulphuric acid; in this way the acid is obtained in a crystalline state. The crystals may be heated to 302° without alteration, but at a higher temperature they are decomposed.

This acid forms both an acid and neutral class of salts, the first containing one atom of water and one atom of metallic oxide as base, the other two atoms of metallic oxide. All these salts when distilled with an excess of hydrate of potash leave a residue composed of sulphate and sulphite with carbonate of potash, indicating the presence of hyposulphuric acid in the original compound. *Acid hyposulphobenzoate of barytes* crystallizes in oblique rhomboidal prisms, soluble in 20 parts of cold water, and containing 9.6 per cent of water of crystallization or 3 atoms, which it loses at 212° .

Neutral hyposulphobenzoate of barytes, $2\text{BaO} + \text{C}_{14}\text{H}_4\text{O}_3, \text{S}_2\text{O}_5$; is obtained by boiling the acid salt with carbonate of barytes;

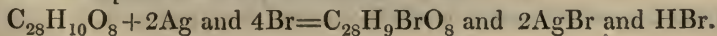
* Proceedings of the Pharmaceutical Meetings at Mr. Bell's, Part 1, vol. 1. 1841.

it is more soluble than the former salt, but crystallizes with difficulty in a regular form. It will be observed that hyposulphobenzoic acid is formed by the abstraction of the elements of 1 atom of water from 1 atom of benzoic acid and 2 atoms sulphuric acid, and that it retains the saturating power of 2 atoms of acid, being bibasic.

Nitrobenzoic or benzoënitric acid, $\text{HO} + \text{C}_{14}\text{H}_4\text{O}_3, \text{NO}_4$; an acid formed by the abstraction of HO from the elements of nitric acid and benzoyl. It is prepared by boiling benzoic acid with an excess of nitric acid, the first is dissolved and colours the fluid red; deutoxide of nitrogen is evolved as an accidental product arising from the action of the nitric acid on the nitrobenzoic acid already formed. From the cold solution crystals similar to benzoic acid are deposited; the fluid eventually becomes a solid crystalline mass. At 50° , 400 parts of water dissolve 1 part of the acid, at 212° 10 parts. It dissolves easily in alcohol and ether; fuses at $260^\circ.6$ (127° centig.), but begins to sublime at 230° ; the pure acid sublimes unchanged; chlorine has no action upon it.

The *nitrobenzoates* are for the most part soluble in water and alcohol, crystallizable, explode by heating, and when gently warmed give off nitrobenzide ($\text{C}_{12}\text{H}_5\text{NO}_4$). *Ammonia* forms a neutral and acid salt. The salt of *lime* is acicular and contains 2 atoms of water, which are driven off at 374° . The salt of *barytes* loses 4 atoms of water at 212° . The salt of *strontian* loses $2\frac{1}{2}$ equivalents of water at 266° . When acid nitrobenzoate of ammonia is added to a solution of sulphate of zinc, a gelatinous basic salt precipitates, containing 4 atoms of *oxide of zinc* to 1 atom of acid. The filtered solution gives the neutral salt of zinc in crystalline plates, which contain 5 atoms of water. The salt of *copper* is a blue powder soluble in hot water, containing 1 atom of water. Besides a neutral nitrobenzoate of *lead*, a remarkable sub-salt exists, in which 1 atom of oxide of lead is united with 5 atoms of the neutral salt. Nitrobenzoic acid forms fine crystallizable compounds with both oxide of ethyl and oxide of methyl. (Mulder, Mitscherlich.)

Bromobenzoic acid, $2\text{HO} + \text{C}_{28}\text{H}_9\text{BrO}_8$; a bibasic acid, discovered by Peligot, and formed by the action of 4 atoms of bromine upon 2 atoms of benzoate of silver:

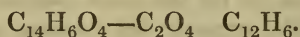


When bromobenzoic acid is precipitated from its salts by a strong acid, the latter assumes the two atoms of water of the bromobenzoic acid, which is thrown down anhydrous. The bromobenzoates are in general crystallizable salts, that of the peroxide of iron is insoluble, and has the properties and appearance of the benzoate of iron.

BENZOLE.

Syn. *Benzin*, *benzene*, *phene*. Formula $C_{12}H_6$.

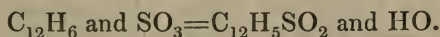
This compound, which is named benzole by Liebig, the termination *ole* being assigned to hydrocarbons, was originally obtained by Mr. Faraday from the condensed liquid of compressed oil gas and described under the name of bicarburet of hydrogen; more lately Mitscherlich found that it was the principal product formed on distilling benzoic acid with hydrate of lime, and named it benzin. By the abstraction of the elements of 2 atoms of carbonic acid from 1 atom of crystallized benzoic acid:



Benzole is prepared by distilling 1 part of crystallized benzoic acid with 3 parts of hydrate of lime; rectifying the oily product by a second distillation with water, or better from quicklime. It is a limpid colourless liquid, of a peculiar ethereal odour which is agreeable; its density is 0.85; it boils at $186^{\circ}.8$ (86° centig.); the density of its vapour is 2378, its combining measure 4 volumes; at 32° it becomes a crystalline mass, which becomes liquid at $44^{\circ}.6$ (7° centig.) Benzole, is insoluble in water, soluble in alcohol and ether. It is not decomposed by any hydrated acid.

Sulphobenzide, $C_{12}H_5SO_2$ (Mitscherlich). Benzole like naphthaline affords several products when decomposed by acids. When exposed to the vapour of anhydrous sulphuric acid it forms a viscid liquid, which dissolves entirely in a small quantity of water; on adding a larger quantity of water, sulphobenzide falls as a precipitate, which, dissolved in ether, gives sulphobenzide crystallized, by evaporation. Sulphobenzide is a colourless substance, perfectly neutral; it fuses at 212° , boils

at a higher temperature and sublimes unchanged. In the formation of this substance 1 atom of anhydrous sulphuric acid and 1 atom of benzole abandon 1 atom of water :



Hyposulphobenzidic acid, sulphobenzinic acid, benzosulphuric acid, $\text{HO}, \text{C}_{12}\text{H}_5\text{S}_2\text{O}_5$; this acid remains in the liquid which deposits sulphobenzide. It is also produced on dissolving benzole in oil of vitriol, or in fuming sulphuric acid. It is a very acid liquid, which crystallizes, and resists a temperature of 392° . It may be viewed as a compound of sulphobenzin with hydrated sulphuric acid. *Hyposulphobenzidate of copper* forms large regular crystals. (Mitscherlich).

Nitrobenzide, $\text{C}_{12}\text{H}_5\text{NO}_4$, a liquid compound obtained by dissolving benzole to saturation in hot concentrated nitric acid; on diluting the acid with water and allowing it to cool, the liquid separates and subsides to the bottom. At 59° nitrobenzide is yellow, has a sweet taste and the odour of cinnamon. Its density is 1.209, that of its vapour 4294; it boils at 433.4° (223° centig.), crystallizes in needles at 37.4° (3° centig.). It is insoluble in water, soluble in alcohol and ether; dilute acids also dissolve it; alkalies do not decompose it. (Mitscherlich).

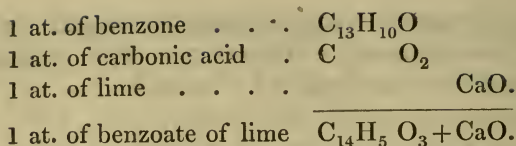
Azobenzide, $\text{C}_{12}\text{H}_5\text{N}$, a volatile, red, crystalline substance, obtained on distilling an alcoholic solution of nitrobenzide with dry hydrate of potash. It is fusible at 149° , and boils at 379.4° (193° centig.).

Chloride of benzole, $\text{C}_{12}\text{H}_6\text{Cl}_6$, a crystalline substance, obtained on exposing benzole to chlorine gas, in sunshine; 6 atoms of chlorine unite with the benzole without displacing any hydrogen. (Mitscherlich).

Chlorobenzide, $\text{C}_{12}\text{H}_3\text{Cl}_3$, an oily liquid, obtained by distilling chloride of benzole from hydrate of lime. It boils at 410° , its density is 1.157, that of its vapour 6370.

Bromine forms analogous compounds with benzole.

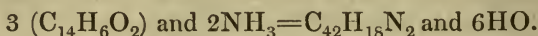
Benzone, $\text{C}_{13}\text{H}_5\text{O}$, one of the liquid products of the distillation of crystallized benzoate of lime :



The crude product of the distillation contains also benzole and naphthaline, of the first of which it is divested by heating it on a water-bath, and keeping it for a sufficient time at 392° , and of the second by exposing the liquid thus obtained to a cold of -4° , when naphthaline separates. Benzene is oily and viscid; not altered by nitric acid and hydrate of potash, but decomposed by chlorine and sulphuric acid. (Peligot).

PRODUCTS OF THE DECOMPOSITION OF HYDRURET OF BENZOYL.

Hydrobenzamide, $\text{C}_{42}\text{H}_{18}\text{N}_2$, or $\text{C}_{14}\text{H}_6\text{N}_3$. Hydruret of benzoyl is acted upon when mixed with twenty times its volume of a concentrated solution of ammonia in a vessel hermetically sealed, and kept for several hours at a temperature of 104° to 122° (40 to 50° centig.). A crystalline mass of hydrobenzamide is formed, which may be purified from the oil by washing with cold ether, in which hydrobenzamide is insoluble, dissolving the residue in alcohol, and evaporating at the usual temperature, when hydrobenzamide is obtained in regular crystals. They are colourless octohedrons or rhomboidal prisms, which enter into fusion at 230° , and are decomposed by dry distillation leaving a residue of charcoal. The alcoholic solution is converted by boiling into ammonia and hydruret of benzoyl. This substance is formed by the abstraction of the elements of 6 atoms of water from 3 atoms of hydruret of benzoyl and 2 atoms of ammonia (Laurent):

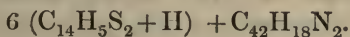


The whole oxygen of the oil and whole hydrogen of the ammonia separate as water; the formation of this substance is, therefore, different from that of an ordinary amide. It is, indeed, simply a hydruret of benzoyl, in which the 2 atoms of oxygen are replaced by N_2 .

Benzhydramide, a crystalline substance, isomeric with hydrobenzamide. *Azobenzoïle*, $C_{42}H_{15}N_2$, or $C_{14}H_5N_{\frac{2}{3}}$; a white crystalline powder, soluble in alcohol. *Benzoïlic azotide*, $C_{14}H_5N$, a white, insipid, crystalline powder, insoluble in boiling alcohol. These three bodies were derived by Laurent from a yellow resinous mass, which is formed by the action of solution of ammonia, upon the crude essence of bitter almonds of commerce.

Hydruret of sulphobenzoyl, $C_{14}H_5S_2 + H$; a body representing the hydruret of benzoyl, of which the 2 atoms of oxygen of the benzoyl are replaced by 2 atoms of sulphur. M. Laurent has generally succeeded in preparing this compound by dissolving 1 volume of the crude essence of bitter almonds in 8 or 10 volumes of alcohol, and then adding gradually 1 volume of sulphuret of ammonium. The liquor becomes turbid in a few minutes, and allows a white powder to fall, similar to farina. By throwing this on a filter, and washing it several times with boiling alcohol, the hydruret of sulphobenzoyl is usually obtained pure. It is white, pulverulent, and composed of small rounded grains, like those of starch, without a trace of crystallization. Although apparently inodorous, it communicates a highly disagreeable odour to the hands. It is insoluble in water and alcohol, slightly soluble in ether. It is slowly decomposed by an alcoholic solution of potash.*

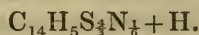
Hydruret of sulphazobenzoyl, a crystalline compound, formed by dissolving essence of bitter almonds in 4 or 5 volumes of ether, adding to it 1 volume of sulphuret of ammonium, and leaving the whole for fifteen days or a month. It forms a white crystalline crust, which it is necessary to dissolve and crystallize from ether to purify it. Its analysis represents a compound of 6 atoms of hydruret of sulphobenzoyl with 1 atom of hydrobenzamide :



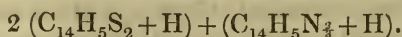
Other views may be taken of the constitution of this substance. On the theory upon which it is named by Laurent, it

* Sur de Nouvelles combinaisons benzoïliques azotées et sulphurées; par M. Laurent.—Annales de Chimie, &c. 3me Série, tome 1, p. 292.

is benzoyl in which the 2 equivalents of oxygen are replaced by 2 equivalents made up of sulphur and nitrogen :



Or, multiplying the preceding formula by three, as 2 atoms of hydruret of sulphobenzoyl, and 1 atom of hydruret of azobenzoyl :



In these formula, $N_{\frac{1}{2}}$ is made equivalent to S or O, an opinion which M. Laurent has long maintained.

Benzimide, $C_{28}H_{11}NO_4$, a substance discovered by Laurent in crude essence of bitter almonds. It crystallizes in white needles, which have a pearly lustre and are very light.

ISOMERIC COMPOUNDS OF BENZOYL.

Benzoïne, $C_{14}H_6O_2$, a crystalline substance, having the same composition as hydruret of benzoyl, into which the latter is often converted in a manner that is not understood. It is never produced in the pure hydruret of benzoyl, but is formed in the essence, which contains hydrocyanic acid, by the presence of alkalies, sulphuret of sodium and cyanide of potassium. The essence may be converted entirely into benzoïne, by mixing it with an equal volume of a solution of potash in alcohol kept cold. It is purified by repeated crystallizations from alcohol.

Benzoïne crystallizes in colourless prisms of high lustre, is inodorous, tasteless, fuses at 248° , and distils at a higher temperature without being modified. It is slightly soluble in hot water, but insoluble in cold, more soluble in hot than cold alcohol.

Hydrobenzoïnamide, a white powder, obtained by treating benzoïne with solution of ammonia at a gentle heat, isomeric with hydrobenzamide (Laurent).

Benzile, $C_{14}H_5O_2$, a substance which crystallizes in regular six-sided prisms, of a rhombic base, and sulphur-yellow colour; formed by passing a stream of chlorine gas through fused benzoïne, so long as hydrochloric acid is disengaged. It is ino-

dorous, tasteless, fuses between 194 and 197° (90 and 92° cent.). May be distilled, or dissolved in concentrated sulphuric acid without change. The aqueous solution of potash has no effect upon it, but the alcoholic solution converts it into benzilic acid (Laurent).

Benzilic acid, $\text{HO} + \text{C}_{28}\text{H}_{11}\text{O}_5$; may be separated from benzilate of potash by an excess of hydrochloric acid. The acid crystallizes on cooling, in colourless rhombohedrons, of high lustre, or in long prismatic needles. It fuses at 248°, and is decomposed at a higher temperature, giving a sublimate of benzoic acid, accompanied by violet vapours, and a residue of carbon. It forms a lively crimson solution in cold oil of vitriol. Benzilic acid contains the elements of 2 atoms of benzile and 2 atoms of water, one of which remains basic to the acid, and is replaced in the benzilates by a metallic oxide. *Benzilate of potash* forms large limpid crystals, soluble in water and alcohol. (Liebig).

Azobenzoïde, $\text{C}_{42}\text{H}_{16\frac{1}{2}}\text{N}_{2\frac{1}{2}}$; a white pulverulent substance, described by Laurent, but of which the composition is rather doubtful.

Cyanobenzile, a substance which is deposited in transparent, voluminous crystals, when to an alcoholic solution of benzile, one third of its bulk of very concentrated hydrocyanic acid is added, and the whole gently heated. (Von Zinin).

SYNAPTASE.

The white of both sweet and bitter almonds consists, in a great measure, of a peculiar matter, very soluble in water, which was named synaptase by M. Robiquet. To prepare it, he directed sweet almonds, from which all the fat oil has been expressed, to be mixed intimately with twice their weight of water, allowed to macerate thus for two hours, and then to be submitted to pressure, which is uniformly increased. The filtered liquid contains vegetable albumen, which is thrown down by acetic acid, and gum, which is precipitated by acetate of lead. A liquid remains, which contains some free acetic acid, acetate of lead, sugar and synaptase; the lead is thrown down by sulphuretted hydrogen, and the synaptase by alcohol, while the free acid and sugar remain in solution. The precipitated

synaptase is washed with alcohol, and dried in vacuo over sulphuric acid.

Dry synaptase is described as a yellowish white, opaque, horny mass, hard and friable; very soluble in cold water. In a fresh solution, iodine produces a deep rose colour, without any precipitate. The solution of synaptase does not keep, but soon becomes turbid from the formation of a white precipitate, and acquires a mouldy odour. It is precipitated from solution by alcohol, in flocks, which redissolve in an excess of water. Acids do not produce a precipitate in its solution; at 140° it coagulates like albumen. It contains azote, and produces ammonia and a new acid in boiling solutions of the alkalies. The composition of synaptase has not been determined.

A matter which, if a pure substance, is probably the same was obtained by Liebig and Wöhler, and named *emulsin*, by treating an emulsion of sweet almonds with ether, to take up all the fat oil, and then precipitating the transparent, syrupy liquid which remained, by alcohol, a white matter was abundantly thrown down, which formed, when dry, a horny, semi-transparent mass. This substance gives much ammonia when boiled with a solution of barytes or a caustic alkali. There are no means of determining the atomic composition of emulsin, but the following are the results of two analyses of it by Dr. R. D. Thomson and Mr. Richardson:

Carbon	. . .	49.025	48.555
Hydrogen	. . .	7.788	7.677
Oxygen	. . .	24.277	25.026
Nitrogen	. . .	18.910	18.742
		100.000	100.000

The reaction which occurs when synaptase and the amygdalin of bitter almonds meet each other in solution is very remarkable, and a knowledge of it necessary to enable us to form a conception of the phenomena of the distillation of the bitter almond. I shall state here the latest view of it which has been taken by M. Liebig. On mixing a solution of 10 parts of amygdalin in 100 parts of water, with a solution of 1 part of synaptase in 10 parts of water, a particular decomposition immediately takes place; the mixture becomes opalescent without losing its

transparency; acquires the odour of bitter almonds, and gives on distillation hydrocyanic acid and hydruret of benzoyl with the vapour of water. The residue is rendered turbid by coagulated synaptase, and on continuing the evaporation, a very sweet liquid is obtained, which contains crystallizable sugar. After destroying the sugar by fermentation, a fixed acid remains in the residue. The quantity of sugar obtained is more considerable than what the elements of the amygdalin could produce; it would appear, therefore, that the elements of the synaptase contribute to its formation. The decomposition is not complete unless the amygdalin and synaptase are dissolved in a proper quantity of water; if it is insufficient to dissolve the hydruret of benzoyl liberated, a corresponding quantity of amygdalin remains undecomposed. (*Traité*, p. 276).

The constituents of the bitter almond are the fixed oil, which is separated by expression, and the synaptase and amygdalin, the two last in such a condition that they cannot re-act upon each other. When the almond cake is treated with boiling alcohol, the amygdalin is dissolved out, and the synaptase coagulated. When the cake is moistened with water, the odour of hydrocyanic acid, and of the essence are immediately perceived, but the cake must be diffused through a certain quantity of water, in order that the mutual action of the synaptase and amygdalin may be complete, and that the whole of the last may disappear. In preparing the *distilled water of bitter almonds* of pharmacy, M. Liebig recommends that a mixture of 1 part of the cake and 20 parts of luke-warm water be made, and left to itself for twenty-four hours before submitting it to distillation.

One atom of amygdalin contains the elements of (Liebig):

1 equiv. of hydrocyanic acid . . .	C ₂	H	N	
2 equiv. of hydruret of benzoyl . . .	C ₂₈	H ₁₂		O ₄
½ equiv. of sugar	C ₆	H ₅		O ₅
2 equiv. of formic acid	C ₄	H ₂		O ₆
7 equiv. of water		H ₇		O ₇
<hr/>				
1 equiv. of amygdalin	C ₄₀	H ₂₇	N	O ₄₂

One hundred parts of amygdalin are said to yield 47 parts of

the crude essence of bitter almonds, and these 47 parts to contain 5.9 parts of free hydrocyanic acid. The last acid is not indicated by nitrate of silver added to a solution of the crude essence in water, owing to the presence of the oil; to obtain a precipitate of cyanide of silver, ammonia-nitrate of silver must be used, and the ammonia saturated with nitric acid, after the lapse of some time.

Laurel-water is prepared by distilling with water 2 parts of fresh leaves of the *prunus laurocerasus*, of which the three first portions are received; the product contains the same elements as the water of bitter almonds. The leaves contain amygdalin and another substance, which appears to act upon it when distilled with water, in a manner analogous to synaptase.

CHAPTER V.

ESSENCE OF CINNAMON AND BODIES DERIVED FROM IT.

CINNAMYL SERIES OF COMPOUNDS.

Cinnamyl, $C_{18}H_7O_2=Ci$; the hypothetical radical of the essence of cinnamon and of cinnamic acid.

Essence or oil of cinnamon.—According to the recent determinations of M. Mulder, $C_{20}H_{11}O$ is the formula for oil of cinnamon derived from the cinnamon of Ceylon, of Java and China, and of the flowers or bark of the cassia-tree. This essence absorbs oxygen from the air, and forms cinnamic acid, two different resins and a new oil $C_{18}H_8O_2$, which appears to be the substance examined, and considered as oil of cinnamon by MM. Dumas and Peligot. The two resins have the composition $C_{30}H_{15}O_4$ and $C_{24}H_{10}O_2$.

This oil is obtained by distilling with water the bark of the *Laurus cinnamomeum*, or the flowers and bark of the cassia. It

is yellow, becoming brown in air, with the odour of cinnamon, and a sweet and burning taste, its density 1.008 at 77°, boiling point 428°; it becomes solid at 23°. It is slightly soluble in water, and the solution produces with iodine and iodide of potassium, reddish brown crystals, of a metallic lustre, containing, according to Dr. Apjohn, $KI + 6(C_6H_5, I)$. The oil dissolves completely in potash, and affords on distillation an oil, lighter than water $C_{18}H_{10}O_2$, while the residue contains cinnamate of potash, and a black matter (Mulder). The bleaching chlorides convert essence of cinnamon into benzoic acid.

Cinnamic acid, $HO + C_{18}H_7O_3 = HO + C_6H_5O$. This acid is formed by the oxidation of the essence of cinnamon in air, or by dissolving the oil of the balsam of Peru in an alcoholic solution of potash, evaporating to dryness, dissolving the residue of cinnamate of potash in boiling water, and liberating the cinnamic acid by an excess of hydrochloric acid. The cinnamic acid crystallizes on cooling in tufts of crystals, which are colourless, and have an aromatic and very acid taste. The crystals fuse at 264°.2 (129° centig.) enter into ebullition at 554°, and distil over as a heavy oil, which fixes on cooling; they sublime at a lower temperature. Cinnamic acid is less soluble, both in cold and hot water, than benzoic acid, which it considerably resembles; very soluble in alcohol and ether; from alcohol it crystallizes in large rhomboidal prisms, which are hard and very friable. It may be distinguished from benzoic acid by nitric acid, which converts it into hydruret of benzoyl and nitro-cinnamic acid; cinnamic acid also does not combine with sulphuric acid as benzoic acid does. The salts of cinnamic acid are monobasic, and have a great analogy to the benzoates. (Dumas and Peligot, Mulder).

Nitro-cinnamic acid, $HO + C_{18}H_6O_3, NO_4$; produced by the abstraction of HO from the elements of cinnamic acid and nitric acid. This acid is prepared by adding cinnamic acid in powder to strong nitric acid, preventing the temperature from rising above 140°. The cinnamic acid is at first dissolved; the mixture soon becomes hot, and a crystalline substance separates; the latter is washed with water, dissolved and crystallized from alcohol. Nitrocinnamic acid is white with a shade of yellow, fuses at 518°; heated above that temperature, it boils and is decomposed. This acid is almost insoluble in

boiling water; it is also but sparingly soluble in alcohol, requiring 327 parts of alcohol to dissolve it at 68° , while cinnamic acid is soluble in 4.2 parts, benzoic acid in 1.96, and nitrobenzoic acid in somewhat less than its own weight.

The alkaline *nitrocinnamates* dissolve easily in water; the other salts are either soluble with difficulty or entirely insoluble; they explode when heated. The *ether* of this acid is formed by heating the latter with 20 parts of alcohol and a little sulphuric acid for several hours, at a temperature not exceeding 176° . The acid is dissolved, and the liquid on cooling deposits the nitrocinnamate of oxide of ethyl in prismatic crystals. This ether melts at $276^{\circ}.8$ (136° centig.), and boils at 572° but is then partly decomposed; it is not decomposed by ammonia.

When more than 1 part of cinnamic acid is added to 8 parts of nitric acid, the temperature rises above 140° , and nitrobenzoic acid is formed, with another acid not yet examined. (Mitscherlich.)

Hydruret of cinnamyl, $C_{18}H_8O_2=HCl$; an oily liquid obtained on adding water to the nitrate of hydruret of cinnamyl; discovered by Dumas and Peligot.

Nitrate of hydruret of cinnamyl, $C_{18}H_8O_2+HO,NO_5$; a compound formed on treating the essence of cinnamon of China, with concentrated and colourless nitric acid. The crystals first obtained are purified by pressure in paper, and afterwards crystallized from alcohol; it forms long oblique rhomboidal prisms, perfectly pure and colourless. This compound soon alters by keeping, disengaging nitrous acid and the hydruret of benzoyl; this decomposition is hastened by heating the compound slightly.

Chlorocinnose, $C_{18}H_4Cl_4O_2$.—This name is given by Dumas and Peligot to a chlorinated product of the essence of cinnamon. It is a volatile solid compound, crystalline and colourless at the usual temperature, which enters into fusion at a moderate heat and sublimes without residue. It is neither altered by concentrated sulphuric acid nor by gaseous ammonia.

Oil of the balsam of Peru.—This oil is obtained by treating 2 volumes of the balsam with 3 volumes of a solution of caustic potash of density 1.3, and floats over a dark watery fluid (Stoltz and Wernher). It is purified by distillation. This oil is termed *cinnameine* by M. Fremy. When boiled with an alkali it is transformed into cinnamic acid, and an indifferent

substance to which Fremy has applied the name *peruvine*. This last is an oily colourless liquid lighter than water; its composition is expressed by $C_{18}H_{12}O_2$. Fremy finds the *balsam of Tolu* to contain the same bodies as the balsam of Peru. According to Richter the balsam of Peru contains two different oils, one of which is soluble in alcohol of 75 per cent and is called by him *myriospermine*, the other oil which is insoluble he names *myroxiline*. On treating the first with an alcoholic solution of potash, an acid is formed different in its capacity of saturation, according to Richter, from cinnamic acid, and which he names *myriospermic acid*. Its atomic weight deduced from the salt of silver is 1553.85.

CHAPTER VI.

SALICIN AND BODIES OBTAINED FROM ITS DECOMPOSITION.

SECTION I.

SALICIN.

Formula: $C_{42}H_{29}O_{22} = C_{42}H_{23}O_{16} + 6HO?$ (Mulder).

This neutral crystallizable substance was discovered by Buchner and Leroux in the bark of the *Salix helix*. It is contained in the bark and leaves of all the species of willow which have a bitter taste, and in some poplars. To prepare salicin the fresh bark or dry ground bark is boiled with water till a strong decoction is made; to the concentrated and boiling decoction oxide of lead is gradually added till the liquid is colourless. Gum, tannin and all extractive matters which may interfere with the crystallization of the salicin are thus carried down by the oxide of lead. The oxide of lead dissolved is then removed first by means of sulphuric acid, and then by sulphuret of barium. The liquid is crystallized by evaporation and the salicin made perfectly white by the use of charcoal and repeated crystallizations. The sulphuret of lead which is precipitated in the

process also assists as a decolorising agent. The barks which contain much salicin yield it at once in crystals, when they are exhausted by cold water and the extract evaporated with caution, according to Merck.

Salicin crystallizes in delicate colourless needles of a silky lustre, which have a bitter taste, and no action on vegetable colours. It is persistent in air, loses nothing at 212° , fuses at 248° , and is decomposed by a higher temperature. Salicin is soluble in 5 or 6 times its weight of cold water, in much less boiling water, is very soluble in alcohol, but insoluble in ether and oil of turpentine. It dissolves purple red in concentrated sulphuric acid, a property by which it may be recognised even in the dry bark, the latter being stained red by sulphuric acid when it contains salicin.

Salicin does not combine with acids, nor possess alkaline properties. It is thrown down by the ammoniacal acetate of lead as a white precipitate, in which according to Piria 6 atoms of water belonging to salicin are replaced by 6 atoms of oxide of lead; but according to Ettling, the quantity of oxide of lead is not constant but increases with the washings to which the precipitate is submitted.

Saliretin, $C_{30}H_{15}O_7 + HO$.—When raised to the boiling point with dilute sulphuric or hydrochloric acid, the solution of salicin soon becomes turbid, and allows a yellowish substance to fall having the consistence of a resin, which is saliretin. When prepared with concentrated acids, the product wants the atom of water represented in the formula, or is anhydrous. In this decomposition 1 atom of hydrated salicin is resolved into 1 atom of saliretin and 1 atom of grape sugar, which last is found in solution.

Saliretin is insoluble in water, and precipitated by that liquid from its solution in alcohol, in ether or concentrated acetic acid, in all of which it is very soluble. It is not soluble in ammonia, but is dissolved by the fixed alkalies and precipitated from them by acids. Saliretin is coloured blood-red by concentrated sulphuric acid; by nitric acid it is converted into carbazotic acid. (Piria).

Chlorinated salicin, chlorosalicin.—Two compounds have been obtained by treating a solution of salicin by chlorine, one a

crystalline yellow powder, $C_{42}H_{25}Cl_4O_{22}$, produced at the ordinary temperature; the other formed about 140° , a red oily liquid, $C_{42}H_{18}Cl_7O_{18}$.

Rutilin.—This name is applied by Braconnot to the product of the decomposition of salicin by sulphuric acid. Alkalies change its tint to a deep purple.

SECTION II.

SALICYL SERIES OF COMPOUNDS.

Salicyl, $C_{14}H_5O_4=Sa$; the hypothetical radical of salicylous acid, salicylic acid and some other compounds: equivalent to benzoyl plus 2 atoms of oxygen.*

Salicylous acid, spiroilhydric acid, $H + C_{14}H_5O_4=H,Sa$. This substance was obtained by M. Piria by distilling salicin with dilute sulphuric acid and bichromate of potash, and has been shewn by Dumas and by Ettling to be the principal constituent of the oil obtained by Pagenstecher by distilling the flowers of the Queen of the meadow (*spiræa ulmaria*), and which M. Lœwig had analysed and described under the name of spiroilhydric acid.

The proportions lately recommended by Dr. Ettling for preparing salicylous acid from salicin are :

- 3 parts of salicin
- 3 parts of bichromate of potash
- $4\frac{1}{2}$ parts of concentrated sulphuric acid
- 36 parts of water.

* The name salicyl was applied by Dumas and Piria to this hypothetical radical, which was viewed as a higher degree of oxidation of benzoyl. The oil of *spiræa ulmaria*, or salicylous acid, is represented as the hydruret of this radical, which also exists in combination with potassium, &c., in the salicylites. An objection to and source of some confusion attending this view is that it represents salicyl as a salt radical or halogen body, combining directly with metals, and not as a basyle, like benzoyl, ethyl, and the other radicals with which it is associated.

M. Liebig points to an explanation of the isomerism of salicylous and benzoic acids and their salts, in the circumstance that while benzoic acid is monobasic, salicylous acid may have its equivalent multiplied by 2 or by 3, and be a bibasic or a tribasic acid. This supposition, however is not supported by the density

The bichromate of potash and salicin are intimately mixed, and after pouring over them two thirds of the water, the whole being well agitated in the retort, we add all at once the sulphuric acid previously diluted with the remaining third of the water, and agitate again. A feeble reaction slowly manifests itself, accompanied by a slight disengagement of gas, which lasts about half an hour or perhaps three quarters of an hour, when an ounce is employed for each part ordered; at the same time the liquid assumes an emerald tint and becomes warm. As soon as that reaction has ceased, the retort is placed upon the fire and moderately heated. The water vapour carries over the salicylous acid, which separates after some time. It is purified by washing it with water and rectifying from chloride of calcium. From half a pound of salicin Dr. Ettling obtained two ounces of the oil.*

Salicylous acid is an oily inflammable liquid, colourless or slightly yellow, having a burning taste, and agreeable aromatic odour; of density 1.1731, becoming solid at -4° (Lœwig); it boils at $385^{\circ}.7$ ($196^{\circ}.5$ centig.) when prepared from salicin (Piria), while the oil from the flowers of the *Spiræa* boils at $359^{\circ}.6$ (182° centig.), according to Ettling. The density of its vapour is by observation 4276; by calculation 4260, or the same as that of benzoic acid. It dissolves easily in water, and may be mixed with alcohol and ether in all proportions; its solution in water reddens tincture of litmus, and discolours it after the lapse of some time. It is decomposed by sulphuric acid; also by chlorine, one atom of hydrochloric acid being formed and eliminated, and one atom of chlorine substituted for the hydrogen, as usual. When heated with an excess of hydrate of potash, salicylous acid is converted into salicylate of potash, with an escape of hydrogen gas. Potassium also when slightly heated in it, gives the same products.

Salicylous acid is recognised by producing a violet colour with salts of peroxide of iron, which disappears after some time. In the *salicylites*, the atom of hydrogen of the formula of salicylous acid is replaced by a metal. The salts of the fixed alkalies

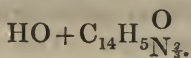
of salicylous acid in the state of vapour, which is the same as that of benzoic acid.

* Liebig's *Annalen* xxxv, 241; or *Annales de Chimie*, &c., 3me Série, t. 1, p. 490.

and ammonia are described as soluble and possessing an alkaline reaction, all the others as insoluble; most of them as yellow and containing water of crystallization. The salts of *lead* and *copper* are anhydrous. The neutral salt of *soda* contains 2 atoms of water which it loses at 248°, the salt of *barytes* contains 2 atoms of water. They are all decomposed by strong acids, and salicylous acid set at liberty. Dr. Ettling describes an acid salt or bisalicylite of potash having the same composition as the bibenzoate of potash; also a corresponding salt of soda, both of which form colourless acicular crystals.

Salicylimide, salhydramide $C_{42}H_{18}O_6N_2$. This body is prepared by dissolving salicylous acid in three or four times its volume of cold alcohol, and adding a quantity of aqueous solution of ammonia, equal to that of the salicylous acid employed. Yellowish white needles are immediately produced, and the liquid soon becomes a solid mass. By a gentle heat the whole is re-dissolved and crystals of salicylimide are deposited on cooling. This body is insoluble in water; it is soluble in 50 parts of boiling alcohol, but very slightly soluble in cold alcohol; its solution has a strong alkaline reaction. Solutions of alkalies and acids act upon salicylimide, with the aid of heat, as they do upon amides, reviving the ammonia and acid.

In the formation of this compound 3 atoms of salicylous acid unite with 2 atoms of ammonia, while 6 atoms of water containing all the hydrogen of the ammonia are abandoned; 2 atoms of nitrogen are thus substituted for 6 atoms of oxygen, in the formation of salicylimide. It may be represented as $3HO + C_{42}H_{15}N_2O^3$, or dividing by three:



Salhydramidide of copper, $C_{14}H_6NO_2Cu$; or $H, C_{14}H_5NO + CuO$. This remarkable compound is represented in the last formula as a salicylous acid, in which 3 atoms of oxygen of the salicyl are replaced by 1 atom of nitrogen, and this is combined with 1 atom of oxide of copper. It is obtained in a state of purity on mixing a solution of salhydramide, the preceding compound, very dilute and slightly cooled, with the ammoniacal acetate of copper. The liquid

immediately assumes an emerald green colour, and soon deposits very brilliant plates of the same colour while at the same time the liquid becomes colourless. When this salt is heated with concentrated acids, it gives a salt of copper and an ammoniacal salt, while the hydrated salicylous acid is set at liberty. Potash ley does not decompose this salt except imperfectly; sulphuretted hydrogen not more completely, even after one or two hours' action. If, however, it has first been made to boil with an acid, the decomposition by sulphuretted hydrogen is instantaneous.

Salhydramidide of iron, $3(\text{H}, \text{C}_{14}\text{H}_5\text{NO}) + \text{Fe}_2\text{O}_3$. This compound, which Dr. Ettling succeeded in forming, is analogous in composition to the copper compound. It precipitates in red flocks, which gradually acquire some lustre, becoming granular. Hydrochloric acid does not alter it in the cold, but when the acid is pretty concentrated and assisted with heat the compound is dissolved and salicylous acid separated.

Salhydramidide of lead. There appear to be two compounds of salhydramide with oxide of lead, but they have not been obtained in a state of purity.

Melanic acid (anhydrous), $\text{C}_{10}\text{H}_4\text{O}_5$. Salicylite of potash exposed in a humid state to air absorbs oxygen and undergoes decomposition, becoming first green and then black. The only products are acetate of potash and an insoluble black powder resembling lampblack, which Piria terms melanic acid. This acid contains no water of combination; it is soluble in alcohol and ether, and very soluble in alkalies.

Salicylic acid, $\text{HO} + \text{C}_{14}\text{H}_5\text{O}_5 = \text{HO}, \text{SaO}$. This acid is produced by heating salicylous acid with an excess of dry hydrate of potash, till the brown mass becomes white, which is attended with the escape of hydrogen gas. The salicylic acid is liberated by adding an excess of hydrochloric acid, and is purified by repeated crystallizations. This acid crystallizes both from solution and sublimation very much like benzoic acid. It may be volatilised without decomposition. It is sparingly soluble in cold water, very soluble in hot water and in alcohol. It reddens vegetable colours and decomposes the alkaline carbonates. *Salicylate of silver* is an insoluble white precipitate, anhydrous. (Piria).

Chlorosalicylic acid, chloride of salicyl, chloride of spiroële;

$C_{14}H_5O_4Cl$. This compound is formed by passing a current of dry chlorine through dry salicylous acid. It crystallizes in yellowish oblique rhomboidal tables of a pearly lustre and peculiar aromatic odour. It fuses and sublimes unaltered. It combines directly with the alkalies, and is precipitated from these combinations by acids without undergoing the smallest change. This acid itself has been compared with the chloro-chromic, and these salts viewed as salicylates of metallic chlorides.

Chlorosalicylimide, chlorosamide, $C_{42}H_{15}Cl_3O_6N_2$; is salicylimide in which 3 atoms of hydrogen are replaced by 3 atoms of chlorine. It is a yellow mass insoluble in water, formed by directing a current of ammoniacal gas upon chlorosalicylic acid, so long as water is disengaged.

Corresponding *bromosalicylic* and *iodosalicylic* acids exist, which undergo the same transformations with ammonia.

Nitrosalicylic acid, spiroëilic acid (Lœwig); $C_{14}H_5O_8N$. Fuming nitric acid has a violent action upon salicylous acid, nitrous fumes are abundantly evolved, with the formation of a dark yellow mass, which volatilises when distilled with water; this matter has not been analysed. When, on the other hand, nitric acid of ordinary strength is digested upon salicylous acid, peroxide of nitrogen is evolved, and a crystalline mass remains, which may be purified by washing it with water and then dissolving it in alcohol. Nitrosalicylic acid crystallizes in small yellow prisms, the alcoholic solution of which dyes the skin and nails yellow; it forms crystallizable salts with the alkalies; ammonia produces with it a deep blood red colour; with the perchloride of iron it assumes a cherry red tint. Its salts have not been sufficiently examined; their probable formula is $MO + C_{14}H_4O_3, NO_4$.

CHAPTER VII.

PHLORIDZIN AND THE BODIES DERIVED FROM IT.

Formula, $C_{42}H_{29}O_{24} = C_{42}H_{23}O_{18} + 6HO$, according to Mulder,

Erdmann, Otto. But $C_{32}H_{15}O_{12} + 6HO$, and when dried, $C_{32}H_{15}O_{12} + 3HO$, according to Stass.

This substance which very much resembles salicin, was discovered by De Kœninck and Stass in the bark of the root of the apple, pear, cherry, and plum tree. It has been considered as crystallized salicin plus 2 atoms of oxygen. It is extracted from the bark cut into small pieces, by digestion in alcohol of 80 per cent, at 176° . It is crystallized by distillation of the alcohol, solution and cooling, and purified by means of animal charcoal.

Phloridzin crystallizes in colourless silky prisms of a square base, of density 1.4298, which are neutral, having a bitter astringent taste, are soluble in 1000 parts of cold water, and in all proportions in hot water, are soluble in alcohol and almost insoluble in ether. Phloridzin loses 4 atoms of water of crystallization at 212° , fuses at 320° , and is not decomposed below 392° (200° centig.). It produces a white precipitate in solution of subacetate of lead. It dissolves a large quantity of hydrate of lime, and gives by evaporation in vacuo a yellow crystalline mass, of which M. Liebig infers the composition to be $C_{42}H_{23}O_{18} + 3CaO, 3HO$, from an analysis by Stass. Phloridzin is a febrifuge like salicin.

Phloretin, $C_{30}H_{15}O_{10}$. When a solution of phloridzin is boiled with a little of any acid whatever, except nitric and chromic acids, it is converted into grape sugar, and the present compound, which separates from the solution as a crystalline powder. Phloridzin thus undergoes a similar change with salicin, by the action of acids.

Nitrophloretic acid, phloretic acid (Stass), $C_{30}H_{12}O_{15}N$; an uncrystallizable matter of a puce colour, obtained by the action of nitric acid on phloridzin. It is soluble in alkaline solutions, and precipitated again by acids.

Phlorizein, $C_{42}H_{29}O_{26}N_2$; a red substance soluble in ammonia, which is obtained by the joint action of air and ammonia on humid phloridzin. The addition of 8 atoms of oxygen and 2 atoms of ammonia to the elements of anhydrous phloridzin, gives exactly the composition of phlorizein. This compound also unites with 1 atom of ammonia, when dissolved in its solution and evaporated in vacuo with sticks of potash, and forms a purple blue powder, of a coppery lustre, very soluble

in cold water, of which the solution has a magnificent blue colour (Stass, An. de Chim. lxi. 367).

CHAPTER VIII.

GLYCERIN.

Glyceryl, $C_6H_7=Gl$; a hypothetical radical admitted by Liebig to exist in the substance long known as glycerin, which is found combined with various acids in the fat oils. Glycerin is considered as a compound of glyceryl with 5 atoms of oxygen and 1 atom of water, or the hydrated oxide of glyceryl.

Hydrate of oxide of glyceryl, glycerin; $C_6H_7O_5 + HO$. This substance was first observed by Scheele, and distinguished by him as the *sweet principle of oils*, its function in the constitution of oils and fats was developed by Chevreul, and its composition carefully determined by Pelouze*. It forms a base to the oleic, stearic, and margaric acids of the fat oils and tallow, and is separated when those acids are made to combine with an alkali or any metallic oxide, in the saponification of the oils. It is conveniently prepared in saponifying oil of olives with oxide of lead and a little water, by boiling them together; the liberated glycerin dissolves in the water, while the soap of oxide of lead is insoluble. The glycerin is accompanied by a small quantity of oxide of lead in solution, which may be precipitated by sulphuretted hydrogen. Or when an oil is converted into a soap by boiling it with water and an excess of alkali, the soap comes to the surface being insoluble in the alkaline liquor. The latter, which contains the glycerine in solution, may be drawn off, the free alkali be neutralised with sulphuric acid, and the solution evaporated to a syrup, from which strong alcohol dissolves out the glycerin. If the product is coloured it may be purified by means of animal charcoal, evaporated by a water-bath, and afterwards in vacuo over sulphuric acid.

* Ann. de Chim. et de Phys. t. 63. p. 19.

Glycerin is thus obtained as a syrup, colourless or slightly yellow and uncrystallizable, inodorous, very distinctly sweet, of density 1.252 to 1.27, attracting moisture from the air, and miscible in all proportions with water and alcohol, but insoluble in ether. It rises in small quantity with the vapour of water, but cannot be distilled without partial decomposition. When heated in air glycerin burns with a luminous flame. It possesses an extraordinary solvent power, scarcely inferior to that of water itself. It dissolves the deliquescent salts, and many other salts which are not deliquescent, as sulphates of potash, soda and copper, nitrates of silver and potash, the alkaline chlorides, hydrates of potash and soda, and the vegetable acids. Nitric acid converts it slowly into oxalic acid; peroxide of manganese with sulphuric acid into formic and carbonic acids. Its solution in water does not undergo any change by keeping, and is not fermentable by yeast. Glycerin is decomposed when boiled with a solution of sulphate of copper, and metallic copper precipitated. It is not precipitated by subacetate of lead, but is itself when hot capable of dissolving oxide of lead. With potash it forms a compound soluble in alcohol; it combines also with barytes.

It is acted upon by chlorine and bromine; the latter forms, with hydrobromic acid, a heavy oily ethereal liquid, $C_{12}H_{11}Br_3O_{10}$, soluble in alcohol and ether. With chlorine, the product is a white solid flocculent substance, $C_{12}H_{11}Cl_3O_{10}$.

Acid sulphate of oxide of glyceryl, sulphoglyceric acid; $HO.C_6H_7O_5 + S_2O_6$. When glycerin is mixed with twice its weight of concentrated sulphuric acid, combination takes place with the evolution of much heat, but without charring. The liquid when diluted and neutralised with carbonate of lime gives a precipitate of sulphate of lime, which is separated by filtration, while sulphoglycerate of lime remains in solution. The acid may be isolated by cautiously precipitating the lime by means of oxalic acid. But it cannot be preserved, for it is gradually decomposed and converted into hydrate of oxide of glyceryl and sulphuric acid; the change takes place still more rapidly when the liquor is slightly heated. Even when newly prepared, this acid liquid precipitates lime and barytes from their salts.

Sulphate of oxide of glyceryl and lime, $CaO.C_6H_7O_5 + S_2O_6$, (Pelouze.) It is deposited from its solution evaporated to the

consistence of a syrup in prismatic needles or colourless plates, which are insoluble in alcohol and ether. The salt of *lead* has a composition analogous to that of lime. The solutions of both of these salts are decomposed by ebullition, and resolved into insoluble sulphates and hydrated oxide of glyceryl.

M. Liebig makes the remark that oxide of glyceryl probably exists in nature combined with other acids besides those of the fats. Thus a *benzoate of oxide of glyceryl* would possess the same composition as picrotoxin; mannite even might be an oxide of glyceryl. (Traité, I. 602.)

CHAPTER VIII.

ETHAL, AND THE CETYL SERIES OF COMPOUNDS.

Spermaceti differs from the other natural fats in affording a peculiar substance, first observed by Chevreul, instead of glycerin, when saponified by an alkali. This substance was named ethal* by MM. Dumas and Peligot, who consider it the alcohol of a new series of compounds, of which the radical is cetyl; or ethal is the hydrate of oxide of cetyl.

Formula of *cetyl* $C_{32}H_{33}=Ct$. Has not been isolated.

Hydrate of oxide of cetyl, ethal; $C_{32}H_{33}O + HO$. To liberate ethal from spermaceti, the latter is digested with an equal weight of hydrate of potash dissolved in 2 parts of water, at a temperature not exceeding 200° for several days. The soap thus formed which consists of oleate and margarate of potash with ethal, is then decomposed by dilute sulphuric acid, which gives a fatty mass, composed of the oily acids and ethal in a state of mixture and not of combination; it is washed well with boiling water, and then boiled with barytes water in excess, which forms insoluble soaps with the oleic and margaric acids; and ethal is dissolved out by means of cold alcohol, which is afterwards distilled off. The ethal is dissolved in ether, to separate a trace of adhering barytic salts.

* A word formed of the first syllables of *ether* and *alcohol*.

Ethal is deposited from an alcoholic solution in crystalline plates; it fuses above 118° , and solidifies at that temperature, forming a white crystalline mass. It is volatile, and may be distilled without decomposition. It is insoluble in water, soluble in alcohol and ether, neutral and does not combine with acids or alkalies. It is decomposed by nitric acid, and combines with sulphuric acid.

Chloride of cetyl; $C_{32}H_{33}Cl=CtCl$.—An oily liquid, formed by the action of perchloride of phosphorus on ethal.

Acid sulphate of oxide of cetyl; $HO.CtO.S_2O_6$.—This compound is formed when ethal is heated with strong sulphuric acid. It forms double salts when neutralised with bases. *Sulphate of oxide of cetyl and potash*, $KO.CtO.S_2O_6$, is prepared by adding an alcoholic solution of hydrate of potash to the preceding compound, sulphate of potash precipitates, and the salt in question remains dissolved in the alcohol, from which it is deposited in white pearly scales. (Dumas and Peligot, *Annales de Chimie*, &c., lxii, 5.)

Ethalic acid, $HO + C_{32}H_{31}O_3$. This compound, the acetic acid of the cetyl series, was formed by M. Dumas, by mixing 1 part of ethal with 5 or 6 parts of the mixture of hydrate of potash and quicklime, and heating to 410° or 428° (210° or 220° centig.), for five or six hours. Hydrogen gas is evolved, and the ethalate of potash formed. The last is decomposed by hydrochloric acid, and the ethalic acid, which separates in flocks, purified by boiling it with the acid liquid, and repeatedly with water, converting it into ethalate of barytes, and treating the last with boiling alcohol, to dissolve out undecomposed ethal. The ethalate of barytes is then decomposed by hydrochloric acid, and the liberated ethalic acid purified by solution in ether.

Ethalic acid is solid, white, inodorous, tasteless, lighter than water. Fused by heat, it solidifies at 101° , and then presents itself in the form of small brilliant needles, in groups radiating from a centre. It is insoluble in water, but is dissolved largely by alcohol and ether. When heated in a little capsule, it boils like ethal, and is volatilised without leaving any residue.

All the *ethalates* are insoluble in water or alcohol, except those of potash, soda, and ammonia. The insoluble ethalates are prepared by precipitating the metallic salts dissolved in

alcohol, by an alcoholic solution of ethalate of potash or soda. The ethalates of the alkalies are decomposed by a large quantity of water, although they dissolve in a small quantity without change. (Dumas and Stas, *An. de Chim. &c.* lxxiii, 124).

Cetene, $C_{32}H_{32}$. This hydrocarbon was obtained by MM. Dumas and Peligot, by distilling ethal repeatedly with glacial phosphoric acid, which deprives the former of 2 atoms of water. It is an oily, colourless liquid, boiling at 527° ; the density of its vapour is, by experiment, 8007; by calculation, supposing its combining measure 4 volumes, 7843. It is insoluble in water, soluble in alcohol and ether.

CHAPTER VII.

OTHER INDIFFERENT SUBSTANCES.

CLASS I. ORDINARY CONSTITUENTS OF PLANTS.

SECTION I.

PECTIN.

Formula: $HO + C_{12}H_{17}O_{11}$. This name was applied by Bracconot to a principle which forms the basis of vegetable jelly.* It is extensively diffused in the juices of pulpy fruits and roots, especially at the time of their maturity, and occasions these juices to coagulate, when mixed with alcohol or boiled with sugar. It may be prepared from apples, for instance, by heating the juice with a little albumen till the latter coagulates, filtering, and precipitating the pectin by a considerable addition of alcohol to the liquid. By a second solution in water, and precipitation by alcohol, the pectin is completely purified. When only a small quantity of alcohol is added to the watery solution, the juice fixes as a jelly after an interval of one or two days.

After being washed on a filter and dried, pectin is semi-transparent, and has a considerable resemblance to isinglass. It

* From *πηκτις*, *coagulum*.

is insoluble in alcohol, soluble in water, the solution is neutral to test paper, insipid or tasteless; it is not adhesive like gum arabic. The dried pectin swells up in water, and more readily in cold than in hot water; with one hundred times its weight of water it forms a jelly, with a larger quantity only a gelatinous liquid. It resembles vegetable mucilage in many of its properties; with nitric acid it first forms saccharic acid, afterwards mucic acid. It is dissolved by an excess of alkali, and converted into the following isomeric acid.

Pectic acid. This substance is conveniently obtained by grating yellow carrots to a pulp, expressing the juice, washing the marc several times successively with distilled or rain-water, and expressing it well again. The marc is then diffused through six times its weight of pure water, free from earthy salts, and solution of pure caustic potash gradually added by small portions. The mixture is then heated and made to boil for about a quarter of an hour, and the boiling liquor filtered through a cloth. The mixture is known to have boiled long enough, when a small portion of it, after being filtered, is found to become a jelly on adding to it a drop or two of acid.

The pectic acid may be separated by a strong acid, but as it is then difficult to wash, it is preferable to precipitate it by chloride of calcium, which gives the pectate of lime, in the form of a coagulated jelly completely insoluble in water. This jelly is washed on a cloth, boiled with water, to which a little hydrochloric acid is added, which dissolves the lime and leaves the pectic acid; the last is then washed with cold water. Pectic acid remains as a transparent and colourless jelly, faintly acid, very slightly soluble in cold water, but more soluble in boiling water. The filtered solution does not become solid on cooling, but it coagulates and forms a jelly when alcohol is added to it, or sugar, which has the property of dissolving pectic acid, and transforming it after some time into a jelly, a property on which is founded the preparation of the jelly of currants, apples, gooseberries, &c.; fruits of which the juice mixed with sugar coagulates in the course of a few days. When evaporated to dryness, pectic acid resembles pectin in appearance, and has the same composition. It is a bibasic acid. The *pectates* possess the property of forming a jelly when precipitated, in common with the acid. Those only containing an alkaline base are soluble in

water, and they dissolve only in the latter when pure and free from acid or earthy salts. (Berzelius, *Traité* II. 367 and 467.)

By boiling it with an excess of caustic alkali, pectic acid is again modified, and converted into another acid, which dissolves easily, is very fluid and has a sour taste. This second acid is also isomeric in its salts with pectin.

SECTION II.

VOLATILE OR ESSENTIAL OILS AND RESINS.

These oils or essences occur in all smelling plants, and are the source of the fragrance of the vegetable kingdom. Some plants, such as thyme, contain a volatile oil in all their parts; in others the oil is confined to particular parts, such as the flower, the pollen, the leaves, the root or the bark. In most plants the oil is contained in little sacs or vesicles, so well closed that the plant may be dried without evaporation of the oil, and the latter is preserved for years from the influence of the air. In other species, and particularly in flowers, the oil is constantly produced at the surface, and dissipated by evaporation the moment of its formation. Essential oils are generally obtained by distilling the plant with water. They are themselves less volatile than water, but are carried over with the steam, owing to the sensible tension of their vapour at 212° , and condensing in the refrigeratory are found on the surface of the distilled water or at the bottom of the vessel. A few oils are obtained by expression, such as those of the oranges and lemons, where the oil resides in the epidermis of the fruit. Some other oils which are not contained in vessels, such as those of violet, jasmine, &c. are obtained by maceration of the flowers in an inodorous fixed oil, and are used in this state in perfumery, or are afterwards obtained apart by distilling the fixed oil with water.

The essences are generally liquid, but occasionally solid at the usual temperature; they have all a strong odour, more or less agreeable, which is somewhat harsh immediately after distillation but improves with keeping, although in general the odour is never so agreeable as that of the fresh plant. Their taste is acrid and burning, or only aromatic when it is greatly weakened

by mixing them with other substances. Some of these essences are colourless, most of them yellow, red or brown, others green, and a small number are blue. They are not unctuous to the touch like the fixed oils, but feel harsh. They produce an oily stain upon paper which disappears on drying. Their density varies from 0.759, the density of oil of coriander, to 1.096, the density of oil of sassafras; but they are generally lighter than water. Although volatile at the ordinary temperature, their boiling point is usually not under 320° . The volatile oils are nearly all decomposed in part when distilled alone. They burn in air with a bright but smoky flame. When exposed to cold they freeze, but generally separate into a solid and fluid portion, indicating that they are mixtures of two oils differing in fluidity; the concrete portion is termed the *steuropten*, and the liquid portion the *elaopten* of the oil.*

The essences exposed to air deepen in colour and absorb oxygen. It has been observed that the odour of oils is closely related with this chemical change. Those which oxidate most rapidly have the strongest smell, and the characteristic odour of no oil can be perceived immediately after its distillation in an atmosphere of carbonic acid gas. The oil becomes in time thick, loses its odour, and is transformed into a resin which in the end becomes hard. A small quantity of carbonic acid is formed in this transformation, but no water; it is greatly promoted by light. An oil which has commenced to undergo this change consists of a portion of oil unchanged, holding a resin in solution, from which the former may be separated by distillation with water. The substance turpentine is in this condition, and gives oil of turpentine, when distilled, with common resin as the fixed residue. Essences should therefore be preserved in well-stopt bottles. They are strongly acted upon and frequently inflamed by concentrated nitric acid. Some of them produce a sort of explosion when mixed with dry iodine.

Essential oils are very slightly soluble in water, but sufficiently so to communicate their odour and taste to that liquid. Water which has been distilled from an odoriferous plant is a saturated solution of the oil; the *distilled waters* used in me-

* These terms were first applied to the solid and fluid portions of fixed oils; they are derived from *στέαρ* suet and *ελαιον* oil.

dicine are so prepared. These liquors are improved by a second distillation, or by keeping for some time in a cool place when contained in opaque vessels imperfectly closed, during which some foreign matters which have been distilled along with the oil, disappear. The volatile oils are all very soluble in alcohol, and the more so the less water it contains. With alcohol of 0.820, oil of turpentine may be mixed in a large proportion, and such a liquid is sometimes burned in a lamp properly constructed for the purpose. The oils which contain oxygen, such as those of lavender and peppermint, dissolve more readily in aqueous alcohol than the pure hydrocarbons. Such solutions of essential oils in alcohol are *lavender water*, *eau de Cologne*, &c. They are rendered turbid by water, which combines with the alcohol and liberates the oil. Essential oils are soluble in ether. They are capable of dissolving at a high temperature a considerable quantity of sulphur and a small portion of phosphorus; and may be combined or mixed with bisulphuret of carbon, chlorides of sulphur, of phosphorus, of carbon and arsenic. They combine with several vegetable acids, such as acetic, oxalic, succinic acids, the oily acids, camphoric and suberic acids. With the exception of oils of cloves, cinnamon and cedar wood, the volatile oils do not combine with salifiable bases; they differ entirely in this respect from the fixed oils which are saponified by alkalies. After being brayed with sugar the volatile oils dissolve better in water. Volatile oils dissolve all the fat oils, resins, and animal fats.

Many volatile oils contain no oxygen, and in all of these, with one or two exceptions, the carbon and hydrogen are C_5H_4 , or some multiple of these numbers; but the larger proportion are oxides. Several of the latter part with their whole oxygen, with a proportional quantity of hydrogen, as water, under the action of anhydrous phosphoric acid, and are converted into pure oily hydrocarbons.

A. ESSENTIAL OILS CONTAINING NO OXYGEN.

OIL OF TURPENTINE.

Formula: $C_{20}H_{16}$. It is derived from several kinds of turpentine, a semi-fluid resin exuding from the different species of the pine. The turpentine is distilled with water, the oil comes

over, and a resin remains behind. The oil met with in commerce generally contains some resin, produced by the oxidation of the oil, from which it should be purified by rectification, that is, a second distillation from water. The pure oil is a colourless, thin liquid, having a peculiar odour, of which the density is 0.872 at 50°, and boiling point 314°.2 (156°.8 centig.) The specific heat of this liquid is 0.462, according to Despretz, that of water being 1.000. The density of its vapour is 5010 by experiment, 4763 by calculation. It abandons only half the heat when condensed from the state of vapour at its boiling point, that vapour of water does at 212°; but a portion of that heat is heat of temperature, for the latent heat of vapour of oil of turpentine is to that of vapour of water only as 0.313 to 1.000. When cooled to -16°.6, oil of turpentine deposits its stearopten in white crystals, which are heavier than water, and fuse at 19°.4 (-7° centig.)

Oil of turpentine is certainly a mixture of two or more isomeric oils; this appears in its forming two compounds with hydrochloric acid, one of which has long been known as *artificial camphor*. To prepare this compound, well dried hydrochloric acid gas is made to pass slowly into the essence surrounded by ice. Without this precaution, it becomes hot, and the hydrochloric acid is not so completely absorbed. It is left to itself for twenty-four hours, after which, a quantity of a white crystalline substance is found deposited in a brown fuming mother-liquor. The composition of the solid hydrochlorate is represented by $C_{20}H_{16} + HCl$. The name *camphene* being applied to the essence by Dumas,* this is the *hydrochlorate of camphene*. When pure, it is a snow-white substance, of a peculiar odour, suggesting that of common camphor, but very different in other respects; fusible above 212°, and volatile; alcohol of 0.806 dissolves at 57° one third of its weight of it. It is decomposed completely when distilled rapidly by means of an oil-bath, with two or three times its weight of quicklime, chloride of calcium being formed, and a colourless oil, of the same composition and density as oil of turpentine, which can be united again with hydrochloric acid, and gives an entirely solid product. This

* The essence of turpentine may be allowed, as the base of artificial camphor, to retain this name.

oil, however, is not identical with the essence, differing from it in its optical properties, and is distinguished as *camphilene* (Deville). The liquid hydrochlorate is of density 1.017, and its composition is also expressed by $C_{20}H_{16} + HCl$. (Soubeiran, Capitaine).

It is difficult to decompose the hydrochlorate of turpentine completely by an alkali; a portion of it distils over and contaminates the oil thus obtained. M. Deville adds gradually to essence of turpentine kept cold, a small quantity, about $\frac{1}{10}$ th of oil of vitriol, so that the whole becomes deep red and viscid after strong agitation, allows it to deposit for twenty-four hours, and decants the thick liquid from a black deposit. This red liquid, when heated, emits some bubbles of sulphurous acid, becomes colourless, and is transformed into a mixture of two oils, which he names terebene (from terebenthine), and colophene. The former distils over first. *Terebene* has the same composition and density as camphene, but differs from the latter in its rotatory power on polarised light being equal to nothing. By treating terebene by hydrochloric acid, Deville obtained a new liquid, *sub-hydrochlorate of terebene*, of density 0.902 at 59° , with a good deal of the odour of terebene itself; its composition $2C_{20}H_{16} + HCl$. A corresponding *hydrobromate* of terebene was a colourless liquid, of density 1.021 at $75^{\circ}.2$ (24° centig.); its composition $2C_{20}H_{16} + HBr$. The solid *hydrobromate of camphene*, formed by the action of hydrobromic acid on the essence is $C_{20}H_{16} + HBr$. It preserves, in common with the solid hydrochlorate, the negative rotatory power of the essence. The liquid hydrochlorate, prepared from the essence, loses that property, and is, therefore, supposed not to contain camphene but terebene, and named *hydrochlorate of terebene*. When hydrochlorate of terebene is distilled with an alkali, it gives an isomeric oil, *terebilene*, having the same relation to terebene that camphilene has to camphene. Two corresponding hydriodates of terebene have been formed.

A very regularly crystallized substance has often been found in old oil of turpentine, or in oil of turpentine left long in contact with dilute nitric acid, which appears to be formed by the assimilation of the elements of water. Its composition is $C_{20}H_{22}O_6$, or represented as a *hydrate* of oil of turpentine $C_{20}H_{16} + 6HO$. (Dumas and Peligot). It is fusible about 302° (150° centig.),

and sublimes. Soluble in 200 parts of cold, and in 22 parts of boiling water, from which it crystallizes on cooling.

By treating terebene by chlorine, M. Deville formed two liquid chlorinated compounds, which he names *chloroterebene*, $C_{20}H_{12}Cl_4$; and *monochloroterebene*, $C_{20}H_{14}Cl_2$. He also formed *bromoterebene*, $C_{20}H_{12}Br_4$. Terebene does not form a hydrate like the essence. The essence treated with chlorine gives a chlorinated compound, which M. Deville names *chlorocamphene*, of the same composition as chloroterebene, but differing in density and other properties.

Colophene is an additional product besides terebene, of the action of concentrated sulphuric acid upon the essence. It distils over after the terebene, on urging the heat so as to bring the viscid mass in the retort to a state of strong ebullition, as a viscid oil, of a clear yellow colour, which re-distilled several times alone, and once (if contaminated with sulphur) from the alloy of potassium and antimony, constitutes colophene. Colophene is colourless by transmitted light, but possesses a kind of dichroism and may be seen of a deep indigo blue colour, a property which can be recognised in all its compounds. Its density is 0.940 at 48°, and 0.9394 at 77°. It is isomeric with the essence of turpentine. Its boiling point is about 590 or 600°; the density of its vapour could not easily be taken with exactness, but was certainly not less than twice that of oil of turpentine. Assuming the density as double, the atom of colophene will be $C_{40}H_{32}$, its combining measure 4 volumes. This oil is also one of the products of the rapid distillation of colophony or the resin of turpentine, and was named colophene on that account.

Colophene absorbs hydrochloric acid, but the *hydrochlorate* is a feeble combination, and is deprived of its acid by chalk. By distilling the impure hydrochlorate from barytes, M. Deville obtained an isomeric oil, which he considers the *colophilene* of colophene. It did not appear, however, to possess the dichroism of the latter body. Colophene also absorbs chlorine with avidity, without any disengagement of hydrochloric acid, and is converted into a resin, soluble in alcohol and crystallizable, having very much the appearance of colophony, and which is named *chlorocolophene*, $C_{40}H_{32}Cl_4$. It is in fact colophony in which 4 atoms of oxygen are replaced by 4 atoms of

chlorine. Fused by heat, and exposed again to chlorine chloro-colophene absorbs that gas, and emits a large quantity of hydrochloric acid, giving a new product, of a transparent yellow colour, which may be represented by $C_{40}H_{24}Cl_8$.

It thus appears that four isomeric oils exist related to the essence of turpentine, of which the common formula is $C_{20}H_{16}$, namely camphene, terebene with camphylene and terebilene, the two latter being obtained by similar processes from the two former; also another pair, of which the atomic weight is double and the formula $C_{40}H_{32}$, namely colophene and colophilene; and that each of these bodies gives rise to a particular series of compounds by uniting with hydrochloric acid, chlorine, &c. (Deville, An. de Chim. lxxv, 37).

COLOPHONY, OR RESIN OF TURPENTINE.

Common turpentine affords when distilled with water from 5 to 25 per cent of essence, what remains being common resin, named colophony, or colophonium, of which the composition generally received is $C_{40}H_{32}O_4$ (Rose); that is, 2 equivalents of the essence combined with 4 equivalents of oxygen. M. Liebig is disposed, from more recent analyses, to represent the resin by $C_{40}H_{30}O_4$, and then in its formation, the essence $C_{40}H_{32}$ loses 2 atoms of hydrogen, which are replaced by 4 atoms of oxygen. The resin is not, however, a homogeneous product, but was divided by M. Unverdorben into two different resins, which he named *sylvic* and *pinic acids*. The properties of the mixture of these resins or colophony are familiar; it is a yellowish brown, translucent, brittle solid, fusible, readily soluble in alcohol, ether, the fixed and volatile oils; soluble in alkaline leys, with which it combines as an acid, and forms soluble salts, which are detergent, and enter largely into the composition of all brown soaps. The two resins are separated from each other by means of cold alcohol, of 72 per cent (sp. gr. 0.867), which dissolves pinic acid, or alpha-resin as it is also called, and leaves behind sylvic acid, or beta-resin.

Alpha-resin (pinic acid), is precipitated from the alcoholic solution by water; it is not crystallizable; after being fused, it has quite the appearance of colophony; it is insoluble in water, but dissolves easily in alcohol, ether, and oil of turpentine;

these solutions have an acid re-action. The pinates of potash, soda and ammonia dissolve in water, but are precipitated by an excess of alkali or the addition of any alkaline salt. The pinates of other bases are insoluble in water, and may be precipitated from alcoholic solutions of the alkaline pinates by double decomposition, employing an alcoholic solution of the other salt; they are most frequently insoluble in alcohol, but many dissolve in ether. The composition of pinic acid was found by Rose to be $C_{40}H_{32}O_4$, or the same as that of colophony ($C_{40}H_{30}O_4$, according to Liebig). Sylvic acid has likewise the same composition.

By distilling or heating pinic acid, a new resin is formed, *colopholic acid*, of the same composition, but possessing a stronger affinity for bases.

Beta-resin (sylvic acid). The insoluble residue treated with boiling alcohol, dissolves entirely; it is filtered hot, and crystallizes on cooling. It is purified by a second crystallization, particularly from alcohol containing a little sulphuric acid. It is transparent and colourless, crystallizes in rhomboidal prisms, terminated by four facets, which are generally very thin, and so large as to resemble tables. It fuses below 212° , is insoluble in water, but dissolves easily in alcohol, ether, the fixed and volatile oils. Alcohol of 72 per cent takes up, when boiling, one third of its weight, but abandons nearly the whole on cooling in a crystalline form. It is dissolved by concentrated sulphuric acid, and precipitated again by water from that solution, but in the condition, according to Unverdorben, of pinic acid. The *sylvates* of *potash*, *soda* and *ammonia* are soluble in water; the *sylvates* of other bases are insoluble in water, but frequently dissolve in ether and even alcohol. The *sylvate* of *magnesia*, in particular, is soluble in alcohol. The addition of ammonia, even in excess, to the solution of sylvic acid in alcohol does not throw down a precipitate, and the acid precipitated by water dissolves readily in ammonia; so also does the resin in caustic potash, but an excess of the latter throws down a *subsylvate of potash*, a compound very slightly soluble in an excess of base. The composition of sylvic acid is $C_{40}H_{30}O_4$, or half these numbers, according to Tromsdorff.

These two resins form the large proportion of colophony, but a third resin has been observed in it, which is indifferent,

soluble in cold alcohol, but not precipitated by the acetate of copper.

The white resin, *galipot*, derived from the *pinus maritima*, consists almost entirely of a colourless, crystallizable resin, named *pimaric acid*, $C_{40}H_{30}O_4$, of the same composition as the preceding resins, but differing from them in properties. When the crystallized resin is dissolved in alcohol, it soon separates as an amorphous powder, which is much less soluble, without alteration in composition. When distilled in vacuo, pimaric acid is converted into another resin, *pyromaric acid*. Boiled for a long time with nitric acid, pimaric acid gives rise to a new acid, containing nitrogen, *azomeric acid*, $C_{40}H_{18}O_{12}N + 4HO$, of which the capacity of saturation is double that of pimaric acid. (Laurent, An. de Chim. lxxii, 383).

By the dry distillation of colophony, M. Fremy obtained a heavy light-coloured oil, almost destitute of taste and smell, boiling above 482° , which he named *resinein*. Its composition is expressed by $C_{20}H_{15}O$; and it appears to be formed by the abstraction of an atom of water from half an equivalent of colophony. By distilling purified resin with eight times its weight of slaked lime, the same chemist procured two liquid products, *resinone* $C_{10}H_9O$, soluble in alcohol, and boiling at $172^\circ.5$; and *resineone* $C_{23}H_{18}O$, less soluble in alcohol, and boiling at $298^\circ.5$ (Liebig, Annalen, xv, 282).

By distilling resin at a higher temperature. MM. Pelletier and Walter obtained a liquid, *retinaphtha* C_7H_4 ; which gives with chlorine a compound $C_{14}H_6Cl_2$. At the same time with retinaphtha, a less volatile liquid, *retinyle*, C_9H_6 , is formed. The less volatile product of the distillation of resin affords a liquid *retinole*, C_8H_4 , with a solid compound *retisterene* or meta-naphthaline, which is isomeric with naphthaline. (Ann. de Chim. &c. lxxvii, 269).

Common resin is converted into shoemaker's resin, or Burgundy pitch, by heating it repeatedly with water, and going to dryness.

Oil of lemons, $C_{10}H_8$. This essence is extracted from the rind of the lemon (*Citrus medica*), usually by expression. The crude oil is pale yellow, but when rectified it is colourless, has a strong smell of lemons, density 0.847, and boiling point

343°.4 (173° centig.). It has absolutely the same composition in 100 parts as essence of turpentine, but only half the atomic weight. It forms, with hydrochloric acid both a solid and liquid compound, according to Blanchet and Sell. The composition of both is expressed by $C_{10}H_8, HCl$. The camphor and also the liquid hydrochlorate of lemon oil are decomposed by means of alkalies, and furnish two oils, which possess the same composition as the essence employed. *Oil of oranges*, from orange-peel (*Citrus aurantium*) differs only in smell from oil of lemons. *Oil of neroli*, or of orange-flower is quite different, and is in great part soluble in water. It appears to contain a stearopten, but its composition is not exactly known.

Oil of junipers.—Obtained by the distillation of crushed juniper-berries with water. It is colourless, and possesses the taste and odour of juniper; is composed of two oils of different volatility, both of them containing carbon and hydrogen in the same relation as all the oils of this class, namely C_5H_4 . By adding a little of this oil to brandy, gin or Hollands are formed.

Savin-oil.—Derived from the berries of *Juniperus sabina*, colourless, also represented by some multiple of C_5H_4 . Both of these oils are used as diuretics.

Oil of copaiba, $C_{10}H_8$. The balsam of copahu or copaiva is extracted in Brazils and the Antilles from several plants, of the genus *copaïfera*. It is obtained by incision, in the same way as common turpentine, with which it has a great analogy; and is a clear-yellow, transparent, thick liquid, consisting of a resin and volatile oil.

The oil is colourless, thin, of an aromatic but disagreeable odour, of density 0.878, and boiling point 473°. Absolute alcohol dissolves two-fifths of its weight of this oil, but twenty-five parts of the spirits of wine of commerce, are required to dissolve one part. It forms a crystallizable compound with hydrochloric acid; it is isomeric with oil of lemons, and has the same mode of condensation. (Blanchet).

Copahuic acid, $C_{40}H_{32}O_4$. This name is applied to the resin of copaiva, which possesses, according to Rose, the same composition as colophony. To obtain it crystallized, M. Schweizer dissolves 9 parts of the balsam in 2 parts of ammonia, and leaves the mixture in a cool place. The crystals which form

being taken out, washed with ether, and re-dissolved in alcohol, furnish the pure resin by spontaneous evaporation; the salt of copahuvic acid and ammonia loses its ammonia during the evaporation. The *copahuvates* of *potash* and *soda* are soluble in water, that of *ammonia* soluble in ether and alcohol, but not in water. The salt of *silver* is crystallizable.

Oil of pepper, from *Piper nigrum*, has the same composition as oil of copaiva, and is similar in properties.

Oil of cubebs, from *Piper cubeba*, is supposed by Soubeiran and Capitaine to be $C_{15}H_{12}$, its compound with hydrochloric acid being $C_{15}H_{13}Cl$. The former is still a multiple of C_5H_4 .

Oil of storax, from the balsam storax liquida, by distillation, has, according to Marchand, its carbon and hydrogen as C_2H , or in the same relation as benzole, and therefore differs in composition from all other known essential oils. It is converted by nitric acid into a resinous body, which yields a particular crystallizable oil, by distillation, the *nitrostyrole* of Simon.

Oil of elemi, obtained by distilling the resin, is a transparent colourless liquid, of an agreeable smell, its density is 0.852 at $75^{\circ}.2$ (24° centig.); it absorbs hydrochloric acid, but does not seem to form a solid camphor. It consists of carbon and hydrogen in the proportion of C_4H_5 . (Stenhouse.)

Laurel-turpentine oil, imported of late from Demerara under the name of laurel oil; its density is 0.8645 at 60° , it begins to boil at 301° , but its boiling point rises to 325° . Its smell slightly resembles that of oil of turpentine, but is much more agreeable and approaches that of oil of lemons. It contains no oxygen, and consists of two or more isomeric oils of the C_5H_4 type. This oil is an excellent solvent of caoutchouc, and is employed as an external application in rheumatism. (Stenhouse.)

B. ESSENTIAL OILS CONTAINING OXYGEN.

Oil of bergamotte is obtained from the ripe fruit of the *Citrus bergamotta*, or *Citrus limetta* (the lime). It is yellowish, but when rectified, colourless, has an agreeable odour, and is much used as a perfume. Its density is 0.862; it combines with hydrochloric acid. It was found by Ohme to contain 7.098

per cent of oxygen, and considered as a hydrate of lemon oil, $3C_{10}H_8 + 2HO$. But MM. Soubeiran and Capitaine find it to be a mixture of 2 or more oils, which differ in volatility, but could not be completely separated, with the proportion of oxygen varying from 3.37 to 16.14 per cent. By the action of anhydrous phosphoric acid upon this essence, an oil is obtained which has the same composition as oil of lemons, or is of the C_5H_4 type. By the action of phosphoric acid on the impure oil a peculiar acid was also produced (named *phospho-bergamic acid*), which forms soluble salts with lime and oxide of lead.

Oil of cloves, from the undeveloped flower-buds of the *Caryophyllus aromaticus*. It is colourless or yellowish, becoming brown in air, of a strong odour and burning taste; its density is 1.061. Clove oil consists of two different oils, one light, of the C_5H_4 type, the other heavy, of density 1.079, and boiling point $469^{\circ}.4$ (243° . centig.) which forms crystalline compounds with bases, and is named *caryophyllic acid*. The two oils are separated by distillation of the crude oil with a solution of potash, by which the heavy or proper clove oil is retained in combination, and may afterwards be liberated by means of sulphuric acid. Alcohol also extracts from cloves a solid substance, *caryophylline*, of which the formula, according to both Dumas and Ettling, is $C_{20}H_{16}O_2$. The distilled water of cloves deposits another substance in yellowish pearly scales, which has been named *eugenine* by Bonastre.

Oil of anise, from *Pimpinella anisum*, is yellowish or colourless, of density 0.9857. It contains so much stearopten that it is solid at the usual temperature.

The stearopten obtained by pressure of the oil cooled to 32° , crystallizes in colourless plates, fuses about 64° , and boils at $431^{\circ}.6$. Its composition, according to the latest determination of M. Cahours, is $C_{20}H_{12}O_2$. With chlorine it appears to form two semifluid compounds of a viscid consistence, $C_{20}H_9Cl_3O_2$, and $C_{20}H_7Cl_4O_2$. With bromine the action is more definite, and a crystalline compound is formed, *bromanisal*, $C_{20}H_9Br_3O_2$. If $1\frac{1}{2}$ parts of sulphuric acid are digested with 1 part of the concrete essence, the latter is entirely converted into a substance of a resinous nature, which when purified from sulphuric acid by distillation, is termed *anisoïne*, by Cahours. It is a per-

fectly white inodorous substance, fusible at a temperature above 212° , of which the formula is $C_{20}H_{12}O_2$, or it is isomeric with the original concrete essence. By the action of dilute nitric acid on the essence of anise, *anisic acid*, $HO + C_{16}H_6O_5$, is formed, which crystallizes in fine needles and is volatile without decomposition; it belongs to the class of benzoic and cinnamic acids. When distilled with an excess of barytes, hydrated anisic acid loses 2 atoms of carbonic acid and yields *anisole* $C_{14}H_7O_2$, a colourless highly mobile liquid, boiling above 302° (150° centig.), of an agreeable aromatic odour, insoluble in water, soluble in alcohol. Anisole gives crystallizable and volatile compounds with chlorine and bromine; it is evidently allied to benzole. Boiled with stronger nitric acid the concrete essence of anise, gives *nitranisic acid*, $HO + C_{16}H_5NO_9$. *Nitraniside* is a yellow resinous substance, produced by the action of fuming nitric acid upon the concrete essence; its probable formula is $C_{20}H_{10}N_2O_{10}$. (Cahours, Ann. de Chim., &c., 3 sér. ii, 274.)

The concrete essences of *fennel* and *badian* are found by Cahours to be absolutely identical with that of anise. The concrete essence of anise is not affected by alkalies, in which respect it differs from camphor, the solid essence of cedar, oil of mint and certain other essences.

Oil of bitter fennel consists principally of two oils, one possessing the composition of the concrete essence of anise; and the other and more volatile oil which is much more difficult to purify, appearing to correspond in composition with essence of lemons and turpentine, but perhaps with a different state of condensation. The more volatile portion, when exposed to a slow stream of *deutoxide of nitrogen*, becomes thick and turbid, and alcohol then throws down from it a white silky matter, of which the composition is $C_{15}H_{12}N_2O_4$. (Cahours.)

Oil of hyssop from the *Hyssopus officinalis*, begins to boil at 288° , but its boiling point rises to 325° . It is a mixture of several oils, one of which probably contains no oxygen, as by repeated rectification of a portion of the oil containing 9 per cent of oxygen with fused potash, the quantity of oxygen was reduced to $1\frac{3}{4}$ per cent, the greater part of the oxygenated oil being converted into a brownish resin. (Stenhouse.)

Cajeput oil, $C_{10}H_9O$, is obtained from the leaves of the *Mela-*

leuca leucadendron of the Moluccas. In the crude state it is green, but becomes colourless by rectification.

Oil of caraways, extracted from the seeds of the *Carum carui*, contains two different oils, one of which is probably a hydrocarbon (Voelkel). These are different from the oils of the *Cuminum cymimum*, although the two plants belong to the same family.

Oil of cummin is extracted from the seeds of the *Cuminum cymimum*. The Roman oil was found by M.M. Gerhardt and Cahours* to consist of two oils. One of these oils they have distinguished as *cymene*; it is a hydrocarbon $C_{20}H_{14}$, and boils at 329° . The other contains oxygen, and appears to be the hydruret of a compound radical like benzoyl, which may be named *cumyl*. Cymene is separated by dropping the essence into hydrate of potash in a state of fusion, the hydrocarbon distils over, and the hydruret of cumyl is retained by the alkali as cuminic acid. The known compounds of cumyl are as follows:

Hydruret of cumyl, or cuminol	. $C_{20}H_{11}O_2 + H$
Cuminic acid	. $C_{20}H_{11}O_2 + O$
Chloride of cumyl or chloro-cuminol	$C_{20}H_{11}O_2 + Cl$
Bromide of cumyl or bromo-cuminol	$C_{20}H_{11}O_2 + Br$
Hydrated cuminic acid	. $C_{20}H_{11}O_2 + O + HO.$

Hydruret of cumyl or *cuminol* is a colourless or yellowish liquid of a strong odour, easily altered by the contact of oxygen when heated. Its boiling point is 428° ; density of its vapour by experiment 5240, by calculation 5094, its combining measure being supposed four volumes. Cuminol is capable of uniting with hydrate of potash at the ordinary temperature without the evolution of hydrogen. It is oxidated and converted into *cuminic acid* by direct oxidation, or when treated with caustic alkali in which case hydrogen is evolved, or by the action of sulphuric acid and chromate of potash. This acid, which corresponds with benzoic acid, is colourless, crystallizes

* Recherches chimiques sur les huiles essentielles. An. de Chim. 3me Série, t. i. p. 60.

in prismatic needles, has an acid burning taste, is scarcely soluble in water, dissolves easily in alcohol, and may be sublimed. When hydrated cuminic acid is distilled with 4 parts of caustic barytes, it yields an aromatic colourless liquid, $C_{18}H_{12}$, to which the name *cumene* has been applied; it boils at $291^{\circ}.2$ (144° centig.) Cumene is analogous to benzin or benzole; it forms with fuming sulphuric acid *sulphocumenic acid*, corresponding with sulphobenzic acid, of which the barytic salt is crystallizable. With nitric acid it forms *nitrocumide*, analogous to nitrobenzide.

Cymene has been found to correspond perfectly in density, boiling point, and density of vapour with *camphogen* from camphor, and is believed to be identical with it. It also appears to be isomeric with *retinylene* from the distillation of resin. It forms a *sulphocymenic acid*.

Lavender oil, $C_{15}H_{14}O_2$ ($=3C_5H_4+2HO$.) This familiar oil is thin, colourless, of density 0.877.

Oil of peppermint from *Mentha piperita* is pale yellow, and lighter than water. It contains a variable proportion of stearopten, so much as sometimes to form a solid prismatic crystalline mass. The composition of the elaopten is $C_{21}H_{10}O_2$; of the stearopten $C_{20}H_{20}O_9$. Phosphoric acid withdraws two atoms of water from the last, and eliminates a liquid hydrocarbon, which M. Walter has named *menthene*, $C_{20}H_{18}$. Distilled with perchloride of phosphorus, the stearopten also gives *chloro-menthene*, $C_{20}H_{17}Cl$. Chlorine is absorbed by the stearopten, and two different chlorinated compounds formed. By the action of nitric acid a liquid acid compound is produced, $C_{10}H_9O_3$. (P. Walter, An. de Chim. lxxii. 83.)

Oil of cedar (solid), $C_{32}H_{26}O_2$, or $C_{32}H_{24}+2HO$. The crude essence as obtained from the cedar wood of Virginia is a soft white crystalline mass, which after being deprived of water by heat becomes solid at $80^{\circ}.6$ (27° centig.) Distilled by a sand-pot heat, it comes over between 527 and 572° (275 and 300° centig.), and separates into a crystalline substance and liquid portion. The solid essence, purified by pressure and crystallization from alcohol is remarkable for its beauty and lustre, its odour is aromatic and peculiar, suggesting that of a cedar-wood pencil. It fuses at $165^{\circ}.2$ (74° centig.), and boils at $539^{\circ}.4$ (282° centig.); it is dissolved very slightly by water, largely by

alcohol, from which it precipitates on cooling in silky crystalline needles. The density of its vapour is by experiment 8400; by calculation 8100, allowing its combining measure to be 4 volumes.

When the concrete essence is distilled with anhydrous phosphoric acid, the latter being added in a gradual manner to prevent great elevation of temperature, a liquid is obtained, *cedrene* $C_{32}H_{26}$, which appears to be the hydrocarbon of the essence. Its odour is aromatic and quite peculiar, its density 0.984, its boiling point $478^{\circ}.4$ (248° centig.); the density of its vapour 7900 by experiment, and 7500 by calculation, supposing its combining measure to be 4 volumes. Sulphuric acid and perchloride of phosphorus act upon cedrene as upon menthene. The liquid essence of cedar, obtained from the crude essence by expression, has the same density and composition as cedrene. (P. Walter, An. de Chim. 3 sér. i. 498).

Oil of roses, otto or attar of roses, is colourless, of a most intense rose odour, lighter than water. Its stearopten, which is inodorous, separates at the usual temperature in large plates; it fuses at 95° , is very slightly soluble in alcohol, and contains no oxygen, but is a polymeric variety of CH.

Oil of mentha viridis is, according to the analysis of Dr. Kane, $C_{35}H_{28}O$.

Oil of valerian, extracted from the *Valeriana officinalis*, consists of a hydrocarbon and oxidated oil, the last giving, when treated with potash in fusion, valerianic acid, the same acid as is extracted from the root of valerian, and obtained artificially by the action of potash upon the oil of potatoes.

Oil of chamomile is extracted from the flowers of the *Matricaria chamomilla*; its colour is deep blue. It contains a hydrocarbon and an oxidated oil, the last of which treated with potash in fusion gives valerianic acid. (Gerhardt and Cahours.) The *Anthemis nobilis*, *Arnica montana* and *Archillea millefolium*, yield also blue coloured oils.

Oil of rue, $C_{25}H_{14}O_3$; obtained by distilling fresh plants of the *Ruta graveolens*; is yellowish green, of density 0.837 at $64^{\circ}.4$ (18° centig.); density of vapour by experiment 7892, by calculation 7690, the combining measure being 4 volumes. This oil is soluble in sulphuric acid, and is precipitated by water; hydrochloric acid has no action upon it. (Dr. H. Will in Liebig's Annalen, xxxv. 235).

CAMPHOR.

Formula: $C_{20}H_{16}O_2$, or $C_{20}H_{14} + 2HO$. This essence is brought to Europe chiefly from Japan; it is obtained by distilling the wood of the *Laurus camphora* along with water, and is refined by a second sublimation. It is in white translucent crystalline masses, somewhat tough, but easily pulverised when moistened with alcohol; possessing a peculiar taste and smell, and may be obtained in brilliant crystals of a high refracting power, either by sublimation or from solution in alcohol. It floats upon the surface of water, its density being from 0.9857 to 0.997; fuses at 347° , and boils at $399^\circ.2$ (204° centig.); the density of its vapour is 5317. It evaporates at the usual temperature, a property that contributes to produce the lively movements which small pieces of camphor exhibit upon the surface of pure water. Like all the essential and fat oils, it also possesses a remarkable tendency to diffuse a thin film of its substance over the surface of water, the result of a kind of capillary attraction, in consequence of which a little column of camphor rising out of water is in the course of a short time cut across at the surface of the liquid. The detaching of the substance of the camphor by this force must occasion a recoil, which appears to be the principal cause of the movements of a floating mass. All movement ceases when a drop of any oil is allowed to fall upon and diffuse over the surface of the water. Camphor is easily kindled, and burns with a white flame. It is but slightly soluble in water, one part of camphor requiring about 1000 parts of water to dissolve it; but the solution has the taste and odour of camphor. It is largely dissolved by alcohol, ether and oils. The solution in proof spirit, known as camphorated spirit, is precipitated by water. Camphor forms liquid compounds with nitric acid, acetic acid and hydrochloric acid. When distilled with anhydrous phosphoric acid it loses $2HO$, and yields a pure hydrocarbon, $C_{20}H_{14}$, to which M. Dumas applied the name camphogen.

Camphogen, after being distilled repeatedly from phosphoric acid, is a colourless liquid, of density 0.861 at $57^\circ.2$, and boiling at 347° . The density of its vapour is by experiment 4780; by calculation 4697, allowing its combining measure to contain

4 volumes (Delalande.) Camphogen exists in some essential oils, which are mixtures of a liquid hydrocarbon and an oxidated oil, as the essence of cummin. Camphogen in its chemical relations resembles benzin or benzole and naphthaline.

Hyposulpho-camphic acid, $\text{HO} + \text{C}_{10}\text{H}_{13}, \text{S}_2\text{O}_5$; is formed when camphogen is heated on a water-bath with a slight excess of fuming sulphuric acid; the camphogen disappears without any evolution of sulphurous acid, and an acid is produced analogous to hyposulphobenzic acid, which forms a soluble salt with lead. *Hyposulpho-camphate of lead* crystallizes in pearly plates, which contain 4 atoms of water of crystallization, $\text{PbO} + \text{C}_{20}\text{H}_{13}, \text{S}_2\text{O}_5 + 4\text{HO}$; but are made anhydrous by a temperature of 248° . The salt of *barytes* is similar in constitution. This salt and the salt of *lime* are remarkable for their taste, of which the first impression is very disagreeably bitter, but changes in a minute or two into a sweet and sugary taste analogous to that of liquorice.

Camphogen also forms a white crystallizable compound when acted upon by fuming nitric acid. (Delalande, Ann. de Chim. 3 sér. i, 368).

Camphoric acid, $3\text{HO} + 3\text{C}_{10}\text{H}_7\text{O}_3$. This acid, which is tri-basic, is produced by long digestion or repeated distillation of camphor with nitric acid; and is divested of adhering camphor by uniting it with potash, and decomposing the salt by nitric acid. It forms prismatic crystals, which are inodorous, of a very sour taste; fuses at $145^{\circ}.4$ (63° centig.), and emits then a pungent vapour. It sublimes partially as the anhydrous acid. It is indifferently soluble in water, more readily dissolved by alcohol.

Camphoric acid forms a neutral and acid salt with *ammonia*; the former contains 3 atoms of oxide of ammonium, and the latter 2 atoms of the same with 1 atom of water as base.

Acid camphorate of oxide of ethyl is formed when camphoric acid, alcohol and sulphuric acid are heated together; and is separated by the addition of water. It appears to contain a bibasic camphoric acid, of which the formula is $\text{C}_{20}\text{H}_{14}\text{O}_6$, united with 1 atom of oxide of ethyl and 1 atom of water. The atom of water can be replaced by fixed bases, and a class of neutral salts formed. By boiling the acid camphorate of oxide of ethyl with

water, it is resolved into tribasic camphoric acid, and *neutral camphorate of oxide of ethyl*, $2\text{EO} + \text{C}_{20}\text{H}_{14}\text{O}_6$. (Malaguti).

The matter considered as *anhydrous camphoric acid*, $\text{C}_{10}\text{H}_7\text{O}_3$, is obtained pure by crystallizing in alcohol the product of the distillation of camphoric acid. It forms long flat colourless prisms, which are tasteless and insoluble in water. By continued boiling in water this substance is dissolved, and then appears as the hydrated tribasic acid. (Laurent).

Liquid camphor, $\text{C}_{20}\text{H}_{16}\text{O}$; the elaopten of the *oil of camphor* of commerce. With the same proportions of carbon and hydrogen as solid camphor, it contains only half as much oxygen. The density of the pure oil is 0.91, its boiling point above 212° .

Campholic acid, $\text{HO} + \text{C}_{20}\text{H}_{17}\text{O}_3$. The vapour of camphor is entirely absorbed by a dry mixture of hydrate of potash and lime, between 300 and 400° centig., without the disengagement of any gas, and campholate of potash formed. This acid has the consistence of camphor, is insoluble in water, and easily saturates bases; it is camphor plus 2HO . (Delalande, Ann. de Chim. etc. 3 sér. i. 120.) Campholic acid, distilled with anhydrous phosphoric acid yields a hydrocarbon, $\text{C}_{18}\text{H}_{16}$, $=4$ volumes of vapour. (Delalande.)

Camphrone, $\text{C}_{20}\text{H}_{21}\text{O}$; was obtained by M. Fremy, by dropping fragments of camphor into a porcelain tube containing quicklime heated to redness. It is a light oil, boiling at 167° , soluble in alcohol and ether but insoluble in water.

C. ESSENTIAL OILS CONTAINING SULPHUR.

Volatile oil of mustard, $\text{C}_8\text{H}_5\text{NS}_2$. Both black and white mustard seeds yield a fat oil by expression. The black seed, when distilled with water, gives a remarkable volatile oil, which is not contained in the seed, but is the result of the reciprocal action of water and an albuminous substance in the seed, named *myroazine* by Bussy, upon another crystallizable principle in it, *myronic acid*, which is soluble in water, and appears to be an acid, although little is known respecting it. This oil is the cause of the acidity of black mustard. The application of boiling water to the mustard, of alcohol, acids or alkalies, which coagulate the albuminous body, prevent the formation of the volatile oil.

This volatile oil is colourless, heavier than water, of a pain-

fully intense odour exciting tears, and produces immediately inflammation and blisters when applied to the skin. Its boiling point is $289^{\circ}.4$ (143° centig.). When burned, it produces sulphurous acid. When the oil and an excess of ammonia are put together in a well stoppered phial, the oil in a few days disappears, and a mass of beautiful crystals is found in its place, containing the elements of $C_8H_5NS_2 + NH_3$. This compound is believed by MM. Dumas and Pelouze, who examined it, to belong to the class of amides. Oil of mustard is deprived of all its sulphur by distillation with hydrated oxide of lead, ammonia being formed with sulphuret of lead and another crystalline substance, *sinapoline*, $C_{28}H_{24}N_4O_4$, which also remains in the retort. (Simon).

To this class of essential oils also belong, oil of *horseradish*, from *Cochlearia armoracia* and *C. officinalis*, oil of *garlic*, from *Allium sativum*, oil of *onions*, from *Allium cepa*, oil of *assafœtida*, from *Ferula assafœtida*, oil of *water pepper*, *Polygonum hydropiper*, of *Arum maculatum*; also those of *Lepidium latifolium*, and of *hops*, *Humulus lupulus*.

The substances which follow are allied to the essential oils.

Nicotianine, a volatile fatty matter obtained in minute quantity by distilling tobacco leaves with water. It is bitter and has a strong smell of tobacco.

Asarine, from the root of *Asarum Europæum*, a crystalline substance, fusible in boiling water, volatile, having an aromatic smell and taste resembling camphor. Its composition is expressed by $C_{16}H_{11}O_4$ (Blanchet and Sell.)

Anemonine from *Anemone pulsatilla*, *nemorosa* and *pratensis*; a crystalline substance, $C_5H_2O_2$ (Fehling); forms anemonic acid with barytes (Lœwig.)

Helenine, from *Inula helenium*; obtained by distilling the fresh root with water, or by acting on it with hot alcohol. It is crystallizable in white prisms, melts at 162° , and boils about 530° . Its formula is $C_{14}H_9O_2$ (Dumas), or $C_{15}H_{10}O_2$ (Gerhardt.) With nitric acid and chlorine it yields two compounds, *nitrohelenine*, $C_{15}H_9O_2 + NO_4$, and *chloride of helenine* $C_{15}H_{10}O_2 + Cl_2$. With anhydrous phosphoric acid, helenine yields a hydrocarbon $C_{15}H_8$. (Gerhardt, Ann. de Chimie, etc. lxxii, 163.)

The wood of *Quassia amara* contains a crystalline body, so also do the pods of *Epidendron vanilla*, and the seeds of *Tan-*

ghinia madagascariensis, the last highly poisonous, but none of them has been fully investigated.

Caoutchouc, or *Indian rubber* is the dried milky juice of several trees which grow in South America and the East Indies. The fresh juice was found by Mr. Faraday to contain in 100 parts, 31.7 of caoutchouc, 1.9 of vegetable albumen, a trace of wax, 7.13 of an azotised substance, bitter, soluble of a brown colour in water and alcohol, and precipitable by nitrate of lead, 2.9 of a substance soluble in water, but insoluble in alcohol, and 56.37 parts of water containing in solution a small quantity of a free acid, which precipitated nitrate of lead and coloured persalts of iron green without precipitating them. These substances are dried and included in common caoutchouc, of which the density is 0.9335. Pure caoutchouc carefully prepared from the milk is of density 0.925, transparent and colourless, or of a light yellowish tint in mass. It contains no oxygen, but in 100 parts 87.5 carbon and 12.5 hydrogen, which are nearly in the proportion of C_8H_7 (Faraday).

Caoutchouc is remarkable for its extraordinary elasticity, and its application to remove marks of black lead pencil from paper. It is soluble in pure ether; a small bag of caoutchouc left in common ether for twenty four hours is softened, and may then be greatly expanded by gradually inflating it, so as to become light enough to ascend in the air when filled with hydrogen gas (Mitchell). Caoutchouc when cut into small pieces and well dried at 230° , is dissolved by rectified petroleum, and by the rectified oils from tar; solutions which are extensively used as caoutchouc varnish. Caoutchouc also dissolves in the volatile and fat oils, but loses its elasticity in the latter. Oil of turpentine is often used in the preparation of caoutchouc varnish; to dissolve the caoutchouc, it is said, after it is softened and expanded by the naphtha. To render cloth air and waterproof, Mr. C. Macintosh first applied several coats of this varnish to one side of cotton or woollen cloth, and then bringing the varnished surfaces of two pieces together, passed the double cloth between heavy rollers, by which the two pieces are made to adhere, and the interstitial spaces are completely filled up. The sheet caoutchouc used by chemists is obtained by sawing off a thin slice from a solid block of the material. In forming short connecting tubes of it, the sheet should be folded round the glass tube it is to fit, and the

superfluous edges cut close to the glass by sharp scissors; the fresh surfaces being then brought into contact and pressed together adhere perfectly.

Caoutchouc when heated to about 450° enters into fusion and forms a viscid adhesive mass. Distilled at a higher temperature, it yields a fluid product, which is a mixture of several hydrocarbons, differing greatly in volatility, the most volatile boiling at 90° ; and the least volatile at 680° . According to Himly, all these volatile oils are of the type C_5H_4 , but from their examination by Gregory and by Bouchardat, some of them resemble olefiant gas or C_4H_4 . *Caoutchine* of Himly is of one of these liquids, of which the boiling point was constant at 339° . Messrs. Enderby observed that the liquid distilled from caoutchouc is a solvent of that substance.

RESINS.

From their endless variety, these bodies form one of the most extensive and indefinite classes of vegetable principles. Like the resin of turpentine, which may be taken to represent them, they flow from the tree dissolved in essential oils, which are removed by distillation with water. In the liquid or soft state, they are named balsams, which are all compounds or mixtures, like turpentine, of resin and essential oil. There is every reason to suppose a close relation in composition between the oil and its associated resin, the last being often obviously the product of the oxidation of the former. The oxidation of the oil may occur by the combination of the entire oil as a radical with oxygen, or by the oxidation of hydrogen, and its removal from the oil in the form of water, and the replacement of the hydrogen lost by oxygen, in equivalent proportions. The point is not decided by the analytical information we at present possess, but M. Liebig adopting the following composition for:

Oil of turpentine $C_{40}H_{32}$ or $C_{20}H_{16}$

And for:

Resin of turpentine $C_{40}H_{30}O_4$ or $C_{20}H_{15}O_2$,

prefers to represent the oil as the hydruret of a radical, or as.

$C_{20}H_{15} + H$, which, like the hydruret of acetyl in olefiant gas is capable of combining directly with hydrochloric acid, and forming a double hydruret, $C_{20}H_{15} + HCl$, or artificial camphor. The same hydruret is converted into the resin of turpentine by the oxidation and replacement of its atom of hydrogen by an atom of oxygen, making $C_{20}H_{15} + O$, and the absorption of an additional atom of oxygen by this compound, making $C_{20}H_{15}O_2$.

Every natural resin is a mixture of several resins, quite as the essential oils are mixtures. They are separated from each other by their unequal solubility in hot or cold alcohol, in ether, in potash and carbonate of potash, or the different solubilities of their compounds with metallic oxides in these and other menstrua. M. Unverdorben, who first threw light on the composition of the natural resins, separated from some, five and more resins, all quite distinct substances. They are heavier than water, and become negatively electrical when rubbed. Some of them which are slightly soluble in water, have a bitter taste, but most of them are quite insoluble in water, and tasteless. They are fusible by a temperature above 212° , and are decomposed by a strong heat. Many resins, when dissolved, redden litmus, combine with bases and possess all the characters of acids; some even decompose alkaline carbonates. Others are neutral, and do not combine with bases. A large number of the resins have been examined and analysed by Professor Johnston, to whose memoirs on the resins contained in the late volumes of the Philosophical Transactions, I must refer for information respecting individual resins.

Amber is found in beds of wood-coal, and appears to be altered resin of the trees. It is a brittle, hard substance, usually nearly transparent, sometimes almost colourless, but commonly yellow or even deep brown, and often includes insects. Its density is 1.065. Amber is insoluble in water, alcohol dissolves about one-eighth of it, refusing to dissolve the rest. Alkalies also act only partially on amber. About 10 per cent of amber is insoluble in ether; what remains dissolves in oil of turpentine and naphtha. Amber thus appears to be a mixture of resins and a bitumen. It contains also succinic acid, which is obtained from it by dry distillation.

RESINOUS VARNISHES.

Varnishes are made by dissolving resins in alcohol, or oil of turpentine, or in a mixture of oil of turpentine and a drying oil. These solutions, when spread upon a surface, evaporate, and leave it covered by a thin coating of the resin. To diminish the brittleness of spirit varnishes, a small quantity of Venice turpentine is added, which gives the coating of varnish a certain tenacity, or a little linseed oil, either alone or mixed with oil of turpentine.

The least coloured varnish is that from copal, which is generally prepared by melting that resin, mixing it while hot with a little drying oil, and adding gradually to the mixture oil of turpentine, in quantity equal to the resin.

Lac varnish or *lacker* applied to articles of brass, is made by heating together :

- 8 parts of shell lac
- 4 parts of sandarach
- 1 part of Venice turpentine
- 4 parts of pounded glass
- 60 parts of alcohol.

The use of the pounded glass is simply to assist the solution of the pounded resin by preventing it from agglomerating into a mass, or sticking to the bottom of the vessel. This is an excellent varnish, but has a brown colour.

The varnish usually employed to cover oil paintings, maps and engravings, is made of :

- 24 parts of mastich
- 3 parts of Venice turpentine
- 1 part of camphor
- 10 parts of pounded glass
- 72 parts of oil of turpentine

The paper ought to be covered by a solution of isinglass, and dried, before the application of this varnish, which otherwise will sink into the paper, and make it transparent.

GUM RESINS.

Many plants afford a milky juice when cut or pierced, such as the dandelion and poppy, which when exposed to the atmosphere, becomes solid, and assumes different appearances, according to the plant from which it is derived. These concrete juices form the gum-resins, which are important from their applications in medicine. They are essentially mixtures of resins with gum and an essential oil. They form a milky liquid or emulsion with water, the gum only dissolving, while the resin and oil remain in suspension together with various other matters with which they may be accompanied. Alcohol dissolves only a portion of them; but dilute alcohol is their best solvent, as it takes up both the gum and resin. The dilute alkalies dissolve them completely, leaving nothing but foreign matter. In their number are, ammoniac, galbanum, assafoetida, olibanum, myrrh, euphorbium, bdellium, aloes, scammony, gamboge, opium, lactucarium, upas, and many others. Very few of them have much chemical interest, and their treatment properly belongs to pharmacy.

The resinous acids produced by the action of nitric acid on aloes have lately been studied by Mr. E. Schunk; they are remarkable for their splendid red and yellow colours, and form well crystallized salts. They are *chrysolepinic acid*, $\text{HO} + \text{C}_{12}\text{H}_2\text{N}_3\text{O}_{13}$; *chrysamminic acid*, $\text{HO} + \text{C}_{15}\text{HN}_2\text{O}_{12}$; with *alsetinic* and *aloeresinic acids*. (Liebig's Annalen, xxxix. 1.)

CHLOROPHYL.

This name is applied to the green colouring matter of leaves and plants in general, which is observed floating in their cells in the form of green globules. Ether dissolves the colouring matter of these globules, leaving a colourless substance, of which the nature is unknown. Chlorophyl is prepared by digesting fresh green leaves in ether, distilling off the latter, digesting the green residue in alcohol which dissolves it, distilling to dryness, and then digesting the chlorophyl in concentrated hydrochloric acid. The fine emerald green solution in that acid is precipitated by dilution with water. The precipitated chlorophyl is again digested in a concentrated solution of

potash, and dissolved by the addition of water. On saturating the last solution after filtration, with acetic acid, chlorophyl precipitates pure, in the condition of beautiful green flocks.

Chlorophyl forms, when dried, a bluish green mass, not fusible, insoluble in water, but dissolving of a fine green colour in alcohol, ether, concentrated sulphuric and hydrochloric acids, and precipitated from these solutions by water. Its solution in alkali is green, precipitated by acids and not by water. Chlorine converts it first into a yellow substance, afterwards into a colourless fatty matter. Chlorophyl is intermediate in its properties between a fat and a resin. Exposed to the light of the sun, it becomes yellow, and is probably then identical with *xanthophyl*, the colouring matter of yellow leaves in autumn.

CLASS II.

CONSTITUENTS OF PARTICULAR PLANTS, OR FAMILIES OF PLANTS.

PIPERIN.

Formula, $C_{34}H_{19}NO_6$ (Regnault).

This is a crystallizable principle in both white and black pepper first observed by M. Oersted; but not the cause of the acrimony of pepper, which is due to a peculiar soft resin. Pepper is exhausted by means of hot alcohol, the solution distilled to the condition of an extract, and that mixed with dilute alkali, by which the acrid resin is taken up, and the piperin left undissolved as a greenish powder, to be purified by repeated crystallization from alcohol.

Piperin forms rhomboidal prisms, of which the angles are $85^{\circ}.40'$ and $94^{\circ}.20'$, colourless, tasteless, inodorous, fusible at 212° , not volatile. It is scarcely soluble in water, and but slightly soluble in alcohol; in cold sulphuric acid it dissolves of a deep red colour.

ASPARAGIN.

Formula, $C_8H_7N_2O_5 + 2HO$.

A crystallizable substance, first obtained by Vauquelin and Robiquet, in the juice of asparagus; it exists also in potatoes, liquorice root, and particularly in the root of *Althea officinalis*,

marsh-mallow, from which last it is generally prepared. The root is exhausted by means of cold water, the solution concentrated by evaporation, and left for a long time in a cool place, for the crystallization of the asparagin. It forms pretty large, colourless, octahedral crystals, of a weak taste, soluble in 53 parts of cold water, insoluble in absolute alcohol, but more soluble in rectified spirits of wine than in water. These crystals lose 12.13 per cent of water at 194°.

Heated with acid or alkaline solutions, asparagin is resolved into ammonia and *aspartic acid*, conducting itself thus like an amide. Heated with water alone, under pressure, above 212°, asparagin is converted into the aspartate of ammonia, by the assumption of 1 atom of water. The formula of anhydrous asparamide is $C_8H_5NO_5 + NH_2$.

Aspartic acid, $HO + C_8H_5NO_6$; crystallizes in thin plates, slightly soluble in water, and possessed of weak acid powers.*

SANTONIN.

A crystallizable substance, obtained by Kœhler and by Alms from the seeds of *Artemisia santonica*, or southernwood. It is colourless and destitute of smell, requires between 4 and 500 times its weight of cold, and 250 times its weight of boiling water to dissolve it. It fuses about 276° without loss of weight. The solution of santonin in alcohol reddens litmus, but its acid powers are weak. Its compound with potash, which has been named the *santonate of potash*, is decomposed when its solution is boiled for a few minutes, and the santonin deposited in crystals when the solution cools. It may be combined with other bases, but not without the agency of alcohol. Its analysis gave C_5H_3O , but its atomic weight is supposed to be twelve times as high (Liebig).†

ESCULIN. 2

This substance is derived, by means of hot alcohol, from the chesnut-tree, ash, and probably other barks. It is in thin colourless plates, or a white powder, of a weak bitter taste, not fusible without decomposition. It is sparingly soluble in cold

* Wittstock in Poggendorff's Annalen, xx, 346.

† Tromsdorff Jun. ; Liebig's Annalen, xi, 190.

water. The solution, by exposure to light, acquires a beautiful blue colour, even when the quantity of esculin is very small; the blue tint vanishes with acids, but is revived by alkalies. The composition of esculin is expressed by $C_{16}H_9O_{10}$.

PICROTOXIN.

The substance to which *cocculus indicus*, the fruit of *Menispermum cocculus*, owes its poisonous qualities, was first investigated by Boullay. It is obtained by boiling in alcohol the bruised seeds, after depriving them, by pressure, of the greater part of their fat oil, distilling off the alcohol, and dissolving the remaining extract in boiling water, slightly acidulated, from which the picrotoxin crystallizes on cooling.

It forms colourless, short and thin prisms, is intensely bitter, and not fusible. It is soluble in 25 parts of boiling water, and very soluble in alcohol; does not combine with acids. It is highly poisonous. Its composition is expressed by $C_{12}H_7O_5$ (Regnault).*

ANTHIARIN.

The most deadly of the Upas poisons, employed by the inhabitants of the East Indian Archipelago to poison their arrows, is a gum resin, from the *Anthiaris toxicaria*, of which the active principle, anthiarim, was separated by MM. Pelletier and Caventou. It crystallizes in fine white plates, which are inodorous, sparingly soluble in water, more so in alcohol. It acts in the highest degree as a deadly poison. Its composition is $C_{14}H_{10}O_5$.

CAFFEIN.

A crystalline substance is obtained from coffee, from tea, and from guarana, a prepared mass from the fruit of *Paullinia sorbilis*. To obtain it from coffee, the raw beans, well dried, are reduced to powder, and exhausted by boiling hot water; subacetate of lead is added to the infusion, to precipitate gum and other matters, the liquid filtered, and the excess of lead thrown down from it by sulphuretted hydrogen. After filtra-

* Pelletier and Couerbe; Ann. de Chim. et de Phys. liv, 181.

tion, the liquid is concentrated by evaporation; the caffein crystallizes on cooling, and is purified by a second crystallization. It may be obtained by boiling tea-leaves in water, filtering and proceeding precisely as with coffee, and also from guarana. It is snow-white, and in fine needles, having a silky lustre, which have a very weak bitter taste; does not act upon vegetable colours, and is sparingly soluble in cold water and alcohol. It loses 8 per cent of water at 212° , fuses at 352° (178° centig.), and sublimates at 725° (385° centig.). From its solution it is precipitated only by tannin. Boiled in a solution of caustic potash, it is resolved into carbonic acid, formic acid and ammonia. With sulphuric acid and hydrochloric acid, it forms crystalline compounds. According to the analysis of Liebig, crystallized caffein consists of $C_8H_5N_2O_2 + HO$. The quantity of this substance in different kinds of coffee was found by MM. Robiquet and Boutron to vary; Martinique coffee containing 6.4 per cent, and St. Domingo coffee only 3.2 per cent of caffein. It is evidently not the principle upon which the peculiar properties of either coffee or tea depend.

Caffeic acid was discovered in coffee by Runge. It is a white powder, which yields, when heated, the characteristic aromatic odour of roasted coffee.

Coumarin is a neutral substance, extracted from the Tonka bean, the fruit of the *Coumarouna odorata*, and the flowers of the melilot, *Melilotus officinalis*, which crystallizes in silky needles, or short prisms. Its composition according to M. Henry is $C_{10}H_8O_2$.

Hesperidin, a crystalline substance, obtained by M. Lebreton from the skin of the unripe orange or lemon.

Populin, found by Braconnot, in the bark of the *Populus tremula*, where it is accompanied by salicin. It crystallizes in snow-white silky needles, has a sweet taste, not unlike that of liquorice, requires about 2000 times its weight of cold water to dissolve it, but dissolves in about 70 times its weight of boiling water.*

Plumbagin, discovered in the root of the *Plumbago europea*.

Daphnin, extracted by Gmelin and Baer from the bark of the *Daphne mezereum*, or common mezerion. It is crystalline, colourless, but little soluble in cold water, soluble in alcohol

* Ann. de Chim. et de Phys. t. 44, p. 296.

and ether. Nitric acid converts it into oxalic acid. It is considered by Gmelin and Baer as a body analogous to asparagin.

VEGETABLE ALBUMEN AND LEGUMIN.

When fresh gluten from wheaten flower is digested in hot alcohol, till everything soluble is taken up, *vegetable albumen* is left, of a greyish colour. It is soluble in water, and is coagulated by heat, insoluble in alcohol and ether, and agrees perfectly in properties with animal albumen.

Braconnot observed a peculiar principle in the fleshy cotyledons of the seeds of papilionaceous plants, to which he gave the name *legumin*. Ripe peas, softened with water and reduced to a pulp, gave, when mixed with pure water, a milky liquid, from which starch precipitated, and which retained legumin in solution, seemingly combined with a vegetable acid. When evaporated by heat, the solution does not coagulate, but deposits the legumin by little and little, under the form of diaphanous pellicles. It is purified by washing it, while still moist, with boiling alcohol. It then has a fine white colour, and does not affect litmus paper. Legumin is soluble in water, but insoluble in alcohol. It dissolves very readily in acetic, oxalic, citric and other vegetable acids, but is precipitated from solution, on the contrary, by the mineral acids, which last, form sparingly soluble compounds with legumin. Alkaline hydrates and carbonates also dissolve it with facility, and the solutions froth like a soap.

M. Liebig has lately made the interesting observation that legumin is identical in properties with the animal principle *casein*, and has the same composition. It is also accompanied by the same salts, namely potash, phosphate of potash, magnesia, lime and oxide of iron, as the casein of milk.

NEUTRAL COLOURING MATTERS.

INDIGO.

Formula of blue indigo, $C_{16}H_5NO_2$. (Crum, Dumas).

This important colouring matter exists in the leaves of all the species of the *Indigofera*. It is obtained also from *Nerium tinctorium*, and in small quantity from *Isatis tinctoria* (pastel or woad), and various other plants. In India, the indigofera plants

are cut before flowering, and allowed to steep for nine or twelve hours in a vat, covered with water, in which fermentation occurs with the evolution of carbonic acid and hydrogen gas. A yellow coloured liquor is drawn off into another vat, in which it is beat and stirred till it acquires a blue colour, and the indigo precipitates. It is then drained on calico, placed on proper frames, and strongly pressed by means of screws, cut into cakes of the proper size, and dried.* The plant thus appears to contain the indigo in a very different state from that in which it is ultimately obtained. It is not certain that it can be extracted from the indigofera without fermentation; but Chevreul has shown that it may be extracted from pastel, by treating the latter with hot water free from oxygen, and that the yellow solution thus obtained became blue, and deposited indigo.

The indigo of commerce is of a deep blue, inclining to black; its fracture is earthy and dull, but becomes of a coppery red when rubbed with a hard body, and the more brilliant and like copper the colour developed by friction, the purer is the indigo considered. It is far from being a pure substance, rarely containing half its weight of blue colouring matter, and often much less. Berzelius separated from it; 1, *gluten of indigo*, by digesting indigo in fine powder with a dilute acid, which also dissolves some salts of lime and magnesia; 2, a principle which he has named *indigo brown*, by means of a concentrated solution of caustic potash gently heated; and 3, *indigo red*, by afterwards boiling the indigo repeatedly with alcohol of density 0.830. Indigo blue remains, but is not yet absolutely free from foreign matter.

To obtain it pure, recourse is had to the solution of indigo in the ordinary indigo vat, or the indigo purified by the preceding processes may be dissolved by imitating on a small scale the preparation of the dyer. One part of indigo in an impalpable powder and 2 parts of quick-lime, recently slaked, are mixed, and introduced into a well stopt bottle with about 150 parts of water. To this is then added two thirds of the weight of the lime of crystallized protosulphate of iron in fine powder, or dissolved in a small quantity of hot water. The bottle then being completely full and well closed, is agitated occasionally

* Dr. Thomson's Organic Chemistry, Vegetables, p. 369.

for several hours, and kept in a warm place till the supernatant liquor acquires a yellow colour. The protoxide of iron precipitated by the lime becomes peroxide, taking oxygen from the blue indigo, which in this altered state forms a compound with the lime, soluble in water. When the yellow solution of this compound is poured out or exposed to air, it rapidly becomes blue from the absorption of oxygen, the indigo loses its solubility and precipitates. In the usual process of dyeing, the indigo is fixed by dipping the yarn or cloth in the same solution of indigo, and then exposing it to air; the indigo thus penetrates into the cloth in a soluble state, and is rendered insoluble afterwards by oxidation within its substance, so that it cannot afterwards be washed out. The sediment in the bottle yields more soluble indigo, when agitated again with pure water slightly heated, or with lime-water. The yellow solutions are mixed together and freely exposed to air, with the addition of a little hydrochloric acid to dissolve the salts of lime, and the blue indigo which precipitates is collected, washed upon a filter and dried. It is afterwards washed with boiling alcohol by M. Dumas to take up the *indigo red* of Berzelius.

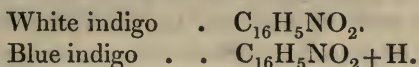
The purified indigo, when dry, is of a deep blue, with a shade of violet, and when rubbed, exhibits a strong copper red colour and metallic lustre. It is tasteless, inodorous, insoluble in water, alcohol, ether, and not affected by alkalies or diluted acids. When heated to about 550° , it fuses (Crum), and at the same time emits a beautiful purple red vapour and sublimes, condensing in small copper-coloured prisms, but it is always partially decomposed at the same time. To observe the beautiful appearance of sublimed indigo, ten or twenty grains of good indigo in powder may be put upon a pretty thick sheet of iron or copper, pressed flat and then covered by the lid of a platinum or porcelain crucible, two or three inches in diameter, while the plate is heated sharply by placing it over a lamp or choffer. On raising the cover, after the plate is cool, the charred mass will be found entirely covered by copper-coloured crystals. Their density is 1.35. Blue indigo was carefully analysed by Mr. Crum,* and repeatedly by M. Dumas, whose results confirm the original determination of Mr. Crum.†

* Thomson's Annals of Philosophy, second series, v. 82.

† Dumas, Ann. de Chim. et de Phys. t. 73, p. 269; and 3 sér. t. 2, p. 204.

White or reduced indigo is produced by the action upon blue indigo of deoxidating bodies of all kinds, such as the protoxides of iron and tin, sulphites and phosphites and many sulphurets, particularly the sulphuret of arsenic or orpiment, but only with the concurrence of an alkali or alkaline earth, which may combine with the reduced indigo. On neutralising a solution of the alkaline compound with hydrochloric acid, carefully excluding air, the reduced indigo is thrown down as a white precipitate, flocculent, and composed of minute crystalline plates. Carefully dried in vacuo, it is coherent, of a greyish white colour and silky lustre; in the dry state it soon becomes blue superficially in the air, but requires several days to become entirely blue. When humid or dry, it is tasteless, inodorous, insoluble in water, soluble in alcohol and ether, which it colours yellow; but it is soon deposited from the alcoholic solution as blue indigo, when exposed to air. White indigo does not affect litmus, dissolves in alkalies without neutralising them, and has not marked acid characters, although it combines with bases. According to the observations of Dumas, the conversion of white into blue indigo occurs in air without any change of weight, or there is, at the utmost a slight but sensible loss.

White indigo was named *indigogen* by Liebig, and blue indigo considered the oxide of that radical. M. Dumas takes another view of the relation between these bodies, considering white indigo not as deoxidised blue indigo, but blue indigo combined with an atom of hydrogen, and forming a hydruret, analogous to the hydruret of benzoyl, thus :



In the oxidation of indigo, on this view, water is formed and liberated. M. Dumas still adheres to this view in his late Memoir on indigo. The combustion of white indigo he found to be easily affected, but that of blue indigo is attended with difficulty, so as to leave some uncertainty as to its composition. According to M. Erdmann, the formula of blue indigo is $\text{C}_{32}\text{H}_{10}\text{N}_2\text{O}_3$.

Action of sulphuric acid.—Indigo combines with fuming

sulphuric acid or oil of vitriol, when slightly heated with that acid in the proportion of 1 to 8, without any evolution of sulphurous acid, and forms a semi-fluid mass, popularly known as *sulphate of indigo*, which dissolves in a considerable quantity of water, of an intense blue colour. The products of this action were first examined by Mr. Crum, whose results form the basis of M. Dumas' later investigations. To convert blue indigo into *sulphindyllic acid*, the latter chemist recommends the digestion of the indigo in a large quantity, not less than 15 parts, of concentrated oil of vitriol, for three days in a bath maintained at a temperature of 120° or 140° . The solution is afterwards diluted with water and filtered, although when these precautions are attended to, little or nothing insoluble remains on the filter. To the limpid liquid a strong solution of pure acetate of potash is added, and the precipitate which falls is washed with acetate of potash, in which salt the sulphindylate of potash is insoluble although soluble in water; the acetate of potash remaining in the precipitate is got rid of by diffusing the latter through a quantity of ordinary alcohol and filtering again. The blue matter remaining when well dried at 212° , gave by analysis, $\text{KO} + \text{C}_{16}\text{H}_4\text{NO}_2\text{S}_2\text{O}_6$; conducting to the following formula for hydrated sulphindyllic acid, $\text{HO} + \text{C}_{16}\text{H}_4\text{NO}_2\text{S}_2\text{O}_6$. Blue indigo thus appears to lose HO in the formation of sulphindyllic acid. *Sulphopurpuric acid*, remains upon the filter in the preparation of sulphate of indigo, when 8 or 10 parts only of sulphuric acid have been employed to 1 of indigo. It is drained, and washed with diluted hydrochloric acid, till the washings are colourless and free from sulphuric acid. It is then carefully dried about 392° (200° centig.). This purple acid gave by analysis, $\text{C}_{32}\text{H}_{10}\text{N}_2\text{O}_4 + 2\text{SO}_3$. The sulphopurpurate of potash is obtained by dissolving the acid in water, and adding acetate of potash to the liquid; it precipitates in purple flocks, which should be washed first with a solution of acetate of potash, and then with alcohol. Its composition indicates that the atom of indigo $\text{C}_{16}\text{H}_5\text{NO}_2$ takes the isomeric state $\text{C}_{32}\text{H}_{10}\text{NO}_4$, to constitute sulphopurpuric acid. M. Dumas institutes the following comparison between the indigo and benzoyl compounds:

$C_{16}H_8NO_2$	Blue indigo	$C_{14}H_5O_2$	Benzoyl
$C_{16}H_8NO_2, H$	White indigo	$C_{14}H_5O_2, H$	Essence of bitter almonds
$C_{16}H_8NO_4$	Isatin of Laurent	$C_{14}H_5O_4$	Salicyl
		$C_{14}H_5O_4, H$	Hydruret of salicyl.

Action of fused potash on indigo.—M. Gerhardt has made the curious observation that when blue indigo is thrown in small portions into fused hydrate of potash, that body dissolves losing its colour, disengaging abundance of hydrogen and ammoniacal gas, and leaving as a fixed residue a mixture of valerate and carbonate of potash. The reaction takes place at the expense of the elements of water; 1 atom of indigo with 14 atoms of water giving 1 atom of valerianic acid, 6 atoms of carbonic acid, 1 atom of ammonia and 6 atoms of hydrogen. On heating the saline residue slightly with sulphuric acid, valerianic acid is obtained in large quantity. This indeed appears to be the most eligible process for preparing that acid.

Indigo is much used in dyeing, being principally applied in the deoxidised state, and forms one of the most permanent colours, resisting every thing except chlorine and nitric acid. In the form of sulphate of indigo, it is used for Saxon blue, which is much less permanent.

Anilic or indigotic acid, $HO + C_{14}H_4NO_9$ (Dumas); is formed when indigo is dissolved in nitric acid considerably diluted, and may be crystallized by concentration of the liquid. It forms colourless prisms, of a sourish bitter taste, fusible and volatile, sparingly soluble in water. It forms crystallizable salts, which detonate feebly when heated. The formula of the salt of silver is $AgO + C_{14}H_4NO_9$ (Dumas). The indigo therefore in forming anilic acid with nitric acid, loses 2 atoms of carbon and 1 of hydrogen.

Picric acid, carbazotic acid, $HO + C_{12}H_2N_3O_{13}$ (Dumas). This acid, which was first known as the *bitter of Welter*, is produced by the action of nitric acid on the preceding compound, and by the solution of indigo or any other azotised organic substance in concentrated nitric acid. It crystallizes in yellow brilliant prisms, of a very bitter taste, which are fusible and volatile, and burn with flame when sharply heated; they are sparingly soluble in water, which they colour yellow. Picric acid is not decomposed by other acids nor by chlorine. Its salts are yellow and generally crystalline; they detonate strongly when sharply heated, or sometimes by a blow, particularly the

potash salt. M. Piria has also observed the formation of picric acid in the treatment of hydruret of salicyl with nitric acid.

Chlorisatin, $C_{32}H_4NClO_3$.* When chlorine gas is transmitted through water in which blue indigo is suspended, hydrochloric acid is formed, and the indigo is converted into a reddish yellow matter, which Erdmann has found to be a mixture of several new products, of which the most remarkable are two chlorine compounds, which have been named chlorisatin and bichlorisatin. When the yellow matter is digested in boiling water, a resin is left undissolved, and a solution formed, which on cooling, deposits a reddish yellow crystalline powder, which is a mixture of the two compounds mentioned. When this is dissolved in boiling alcohol, the chlorisatin crystallizes out first. It forms orange-yellow, four-sided prisms, is bitter, soluble in alcohol, but highly insoluble in cold water. It is partially decomposed by sublimation.

Chlorisatin dissolves in a solution of caustic potash, of a red colour. When heated, the colour of this solution changes to yellow, and a potash salt crystallizes on cooling, in shining plates, of which the composition is $KO + C_{32}H_5NClO_4$. It contains *chlorisatinic acid*, into which, under the influence of bases, chlorisatin is converted, by the fixation of the elements of an atom of water. Strong acids throw down chlorisatin again from the potash salt. The salt of *lead* is a yellow precipitate, which becomes of a fine scarlet on standing. The salt of *copper* is thrown down brownish yellow, but becomes blood-red and granular.

Bichlorisatin, $C_{32}H_4NCl_2O_3$; contains twice as much chlorine as chlorisatin, but greatly resembles it in properties, and is analogous in its relation to alkalies. The salt of lead of its acid is permanently yellow; the copper salt, which first appears as a brown gelatinous precipitate, soon becomes greenish yellow, and then of a splendid blood-red and granular. It is said to form a very fine red on drying, and to take a gold lustre by friction.

Chlorisatyde, $C_{32}H_5NClO_3$; a white substance, which is formed when sulphuretted hydrogen is sent through a solution

* So named from *Isatis tinctoria*. These formulæ are to be considered with reference to the formula ascribed to blue indigo, by M. Erdmann, namely $C_{32}H_{10}N_2O_3$.

of chlorisatin in alcohol; the liquid becomes colourless, and sulphur is precipitated at the same time. Bichlorisatin in similar circumstances yields *bichlorisatyde*, $C_{32}H_5NCl_2O_3$. When treated with potash chlorisatyde and bichlorisatyde yield *chlorisatydic* and *bichlorisatydic acids*.

Chloranile, $C_6Cl_2O_2$, one of the products of the continued action of chlorine upon chlorisatin and bichlorisatin dissolved in alcohol. It is a volatile substance in crystalline scales of a brass yellow colour, which is dissolved by potash of a purple colour, but is then converted into chloride of potassium and chloranilate of potash. *Chloranilic acid* is a reddish powder, composed of fine scales; its composition is C_6ClO_3 .

Chrysanilic Acid, $HO + C_{28}H_{10}N_2O_5$. When indigo in powder is added to a solution of caustic potash, of density 1.35, and boiled in a silver vessel, an orange-yellow salt is formed, without any evolution of gas. The acid is separated as a reddish-brown precipitate on the addition of sulphuric acid to a solution of the potash salt; it is named chrysanilic acid, from its relation to aniline and the golden-yellow colour of its salts. (Fritsche).

Anthranilic Acid, $HO + C_{14}H_6NO_3$. The solution of the fused mass above becomes blue in the air from absorption of oxygen, like a solution of white indigo, and blue indigo precipitates in crystalline grains. On boiling the solution with dilute sulphuric acid, the decomposition proceeds more rapidly, and a brown resinous mass is obtained, soluble in alcohol, ether, and alkalis. To prepare this acid, the first alkaline solution is diluted, and peroxide of manganese added to it in small quantities, at the boiling point, till the solution gives no black precipitate when rendered acid, and its colour is not reddish-brown but a dirty greyish brown. This acid, when sublimed, is white, and resembles benzoic acid, but the fused sublimate is yellow. Its salt of *lime* is very soluble in hot water, and crystallizes in colourless rhombohedrons. Anthranilic acid, distilled by the heat of a spirit lamp, is decomposed in a considerable measure, and resolved into carbonic acid and aniline. (Fritsche; Liebig, *Annalen*, &c., xxxix. 76 and 91.)

Aniline, $C_{12}H_7N$ (Fritsche); an oily liquid, which distils over when finely pulverised indigo is decomposed by a highly concentrated solution of caustic potash or soda in a retort. Its quantity

amounts to about 18 or 20 per cent of the indigo employed. The density of aniline is 1.028, it boils at $442^{\circ}.4$ (228° centig.). Its smell is strongly aromatic, but at the same time disagreeable, it is sparingly soluble in water, but mixes in all proportions with alcohol and ether. Exposed to the air, it acquires a yellow colour, and becomes resinous. The most remarkable property of aniline, is its basic character. It forms salts with acids, assuming an atom of water when it unites with oxygen acids, and combining directly with hydracids, exactly like the vegeto-alkalies and ammonia.

Oxalate of aniline is formed by mingling together alcoholic solutions of aniline and oxalic acid; it falls as a white powder, which is to be washed with alcohol, from which it crystallizes on cooling. Its formula is $C_{12}H_7N + HO, C_2O_3$. *Hydrochlorate* of aniline is prepared by mixing aniline with hydrochloric acid, and crystallizing the salt; it dissolves easily in water; its formula is $C_{12}H_7N + HCl$.*

Unverdorben had previously obtained, among the empyreumatic products of the dry distillation of indigo, an oily alkaline body, which he had distinguished as *crystalline*, because it has the property of forming crystallizable salts with acids. It was not analysed, but there can be little doubt that it is identical with aniline.

COLOURING PRINCIPLES OF ARCHIL, LITMUS, AND CUDBEAR.

Various lichens, which communicate no colour to pure water, strike a fine blue with solution of ammonia. They contain certain crystallizable principles, in themselves colourless, which are thus modified by assuming the elements of ammonia. The history of these principles is still incomplete, although considerable progress has been made in their investigation by the labours of Robiquet, Heeren, Dumas, Kane, and E. Schunk. The limits of this work will not permit me to enter into details respecting the various bodies obtained, of which I can do little more than indicate the names and the composition when determined.

From archil weed, the *Roccella tinctoria*, Dr. Kane obtained the following series of substances, either existing in the lichen,

* Fritsche in Liebig's Annalen, xxxvi, 84.

or produced by the action of re-agents upon principles existing in it.

1. *Erythrilin*, $C_{32}H_{16}O_6$; a white powder, insoluble in water, but converted by ebullition into erythrilin bitter, soluble in alcohol and ether, also in alkaline liquids, from which it is precipitated by an acid; not volatile.

2. *Erythrin*, $C_{20}H_{13}O_9$; sparingly soluble in cold water, but very soluble in boiling water, and separating on cooling in brilliant, micaceous, snow-white scales; the solution is colourless, but in air becomes rapidly brown, and is decomposed. It is very soluble in alcohol, ether and alkaline solutions, from which it is precipitated unaltered by an acid. It fuses at 220° without losing water, and is decomposed at a higher temperature without volatilising. This substance agrees in composition and properties, and is believed by Dr. Kane to be identical with the *pseudo-erythrin* of Heeren, derived from the *Parmelia roccella*. It forms a wine-red solution when exposed to the conjoint action of ammonia and air.

Erythrin bitter, *amarythrin*, $C_{22}H_{13}O_{14}$; is formed when erythrin is dissolved in hot water and exposed some days to the action of air. It is a bitter extractive matter, very soluble in water, much less so in alcohol, and not at all in ether. It is precipitated, like the preceding compounds, by a salt of lead. This is the erythrin bitter of Heeren.

4. *Telerytrin*, $C_{22}H_9O_{18}$; formed when amarythrin, in a semi-fluid state is exposed for several months to air, the latter changing gradually into a mass of very minute granular crystals, of a brownish yellow colour, but becoming white when purified by crystallization from alcohol.

The ordinary *archil* (orseille) of commerce is prepared from the *Parmelia* or *Rocella*. The lichens are reduced to a pulp, and treated with impure ammoniacal liquors. The complete production of archil requires a considerable time, and from Dr. Kane's observations, the colouring matter is in a constant state of transition.

Orcin (cr.), $C_{18}H_{12}O_8$; a colourless crystallizable substance, obtained by Robiquet from the *Lichen dealbatus*. The dried lichen is boiled with alcohol, the solution filtered hot, and distilled to the condition of an extract; the last is exhausted by water, and the concentrated solution brought by evaporation

to a state for crystallization. The orcin is purified by treatment with animal charcoal and repeated crystallization. It forms colourless, four-sided prisms, of a sweet but disagreeable taste, soluble in water and alcohol, easily fused and volatile. Its most characteristic property is the becoming of a deep violet colour, when exposed to the joint action of ammonia and air, owing to the formation of *orcein*. Orcin forms a compound with oxide of lead, of which the formula is $C_{18}H_7O_3 + 5PbO$.

Orcein.—The orcein of archil is of a fine red colour, slightly soluble in water, but colouring it strongly, and wholly precipitated from it by the addition of a neutral salt. It is very soluble in alcohol, which it colours scarlet, and from which water precipitates it. It is scarcely soluble in ether. Orcein dissolves easily in potash or ammonia, giving it a magnificent purple colour, the colour of ordinary archil; from this solution, the colouring matter may be separated by the addition of an excess of common salt. An alkaline orceinate gives with metallic salts, lakes of a fine purple of different shades, which, however, lose much of their lustre in drying. Dr. Kane finds the orcein of archil to be often a mixture of two substances, differing in their proportion with the age of the archil, which he names *alpha-orcein* and *beta-orcein*; the last is produced by the oxidation of the first, and is the orcein of Robiquet and other chemists. Their formulæ are:

Alpha-orcein . . $C_{18}H_{10}NO_5$ (Kane).

Beta-orcein . . $C_{18}H_{10}NO_8$ (Liebig, Kane).

The last was dried before analysis at 212° . The formulæ of their compounds with oxide of lead are: that of alpha-orcein, $C_{18}H_{10}NO_5 + 3PbO$, and that of beta-orcein, $C_{18}H_{10}NO_8 + 3PbO$. The two orceins are identical in all their essential chemical properties; have the same solubility in water, alcohol and ether. The formula of anhydrous orcin being $C_{18}H_7O_3$, that substance requires only to combine with 1 atom of ammonia, together with 2 or 5 atoms of oxygen, to form the one or other variety of orcein.

In addition to the two orceins, the archil of commerce contains *erythroleic acid* and *azoerythrin*, of which the former admits of two modifications; besides the *yellow matter* of Heeren.

Azoerythrin consists of $C_{22}H_{19}O_{22}$ (Kane), by abandoning 4 atoms of carbonic acid and 9 atoms of water, it will yield an equivalent of alpha-orcein.

Erythroleic acid, $C_{26}H_{22}O_8$ (Kane), is a purple substance, distinguished for its semi-fluid consistence at the ordinary temperature, and its solubility in ether and alcohol.

Roccellic acid, $C_{16}H_{16}O_4$ (Liebig), one of the principles extracted by Heeren.

Litmus.—The cubical masses of commercial litmus being reduced to powder and treated with boiling water give a deep blue solution. The mass of insoluble matter, which is of a paler blue than the original substance, is diffused through water and reddened with hydrochloric acid. The whole is then thrown upon a filter, and the red insoluble substance which remains is washed with water until all excess of hydrochloric acid is removed and then carefully dried. The mass when completely dry is boiled in successive portions of alcohol, until every thing soluble in that liquid is taken up. The deep red alcoholic liquors are then distilled in a water-bath to dryness, and the resulting solid material digested in warm sulphuric ether until the latter no longer becomes coloured. The ethereal solutions thus obtained, yield on distillation in a water-bath a fine crimson oily material which is nearly fluid. When purified, this matter forms *erythrolein*, $C_{26}H_{22}O_4$. This compound is completely liquid at 100° ; its solutions in alcohol and ether are of a fine red colour, and it tinges water pink, without however dissolving in any very sensible proportion.

The substance from which the erythrolein has been removed, and which is distinguished by its solubility is *erythrolitmin*, $C_{26}H_{22}O_{12} + HO$; it is of a bright red colour, sparingly soluble in water, which it colours red. It dissolves of a blue colour in potash, and combines with ammonia.

The brownish red mass which resisted the action of alcohol, yields its colouring material but very sparingly to water also; but it may be dissolved in a large quantity of boiling water, and gives by evaporation a deep blood-red mass, consisting of pure colouring material, which has been named *azolitmin*, $C_{18}H_{10}NO_{10}$; it differs only from alpha-orcein and beta-orcein in the proportion of oxygen it contains.

Another substance occasionally but rarely present in litmus is

spaniolitmin $C_{18}H_7O_{16}$. It is of a bright red colour, insoluble in alcohol and in ether, and very sparingly soluble in water, which it tinges bright red.

The blue liquors which are obtained in the first place by digesting litmus cakes in water contain but a small quantity of colouring matter, considering their depth of tint. It is generally azolitmin nearly pure; with occasionally a small portion of spaniolitmin.

By the action of chlorine upon orcein, *chlororcein* is formed, $C_{18}H_{10}NO_8Cl$, which possesses a yellowish brown colour. With azolitmin a similar compound of chlorine is produced, $C_{18}H_{10}NO_{10}Cl$. By the action of nascent hydrogen upon orcein, a colourless body is formed, *leucorcein*, $C_{18}H_{10}NO_8H$. For all these facts we are indebted to Dr. Kane (Phil. Trans. 1840, p. 298).

Cudbear, in German *persio*, is prepared from the *Leconora tartarea*, *Parmelia omphalodes*, and probably other lichens. The lichen is steeped and left for some time in open vessels covered by ammonia, till the purple colour is sufficiently developed, and then the whole is dried in the open air and reduced to a fine powder.

Mr. Schunk has lately obtained by extraction with ether from the *Leconora tartarea* and other lichens employed in the manufacture of cudbear a white crystalline substance *leconorin*, which is dissolved by alkalies and precipitated again unaltered by acids. But if the alkaline solution is allowed to stand for an hour, no precipitate is afterwards obtained, the new substance having resolved itself into carbonic acid and *orcin*. When the solution of the new substance in barytes-water is heated to the boiling point, carbonate of barytes precipitates and the solution yields by evaporation large crystals of orcin. It is probable therefore that orcin does not exist ready formed in any lichen, but is always the product of the action of an alkali, a circumstance which has hitherto been overlooked.

Litmus is much used as a re-agent from its susceptibility to the action of acids and alkalies, being reddened by the former and having its blue colour restored by the latter. In preparing litmus paper an infusion is made of commercial litmus, filtered, concentrated by a water bath, and a very small quantity of carbonate of soda added. Good letter paper cut into slips of

three inches in breadth is dipt into the infusion, allowed to dry and the dipping repeated; or the infusion may be applied to one side only of thin and sized drawing paper. For red paper, the infusion of litmus is acidulated slightly by means of acetic acid. A paper prepared from an infusion of the best cudbear without the addition of either alkali or acid has a purple colour and is affected by both acids and alkalies. It is convenient in alkali-metry, being already too red to be sensibly affected by carbonic acid, while it is distinctly reddened by the mineral acids. The colours from the lichens are beautiful, but fugitive; they are chiefly employed by the dyer to give a bloom to more fixed colours.

COLOURING MATTERS OF MADDER.

Alizarin,* $C_{37}H_{12}O_{10}$ (Robiquet).—This is a crystalline matter of a red colour which was extracted by MM. Robiquet and Colin from the ground roots of madder, the *Rubia tinctorum*. To concentrated sulphuric acid an equal quantity of ground madder is added in a gradual manner, so as to prevent any sensible elevation of temperature; in two or three days nearly all the constituents of the madder are charred and destroyed except the alizarin. The acid is then washed out from the black mass, which is dried and digested with portions of cold alcohol, to take up a fatty matter it contains. The alizarin is afterwards dissolved out by boiling alcohol, the latter solution mixed with water, the alcohol distilled off, and the alizarin which has precipitated is collected on a filter.† It is a red powder, which may be sublimed and is obtained in long flexible capillary needles, having an orange colour; but unless the subliming vessels be very low and flat, almost the whole of the alizarin is decomposed. Alizarin is somewhat soluble in boiling water to which it communicates a rose colour; at 54° , it dissolves in 212 parts of alcohol and in 160 parts of ether. It has a decided affinity for some animal matters, being soluble in albumen, and is precipitated in combination with the latter when coagulated. Phosphate of lime appears also to combine with the colouring matter of madder, from the well known fact

* From *alizari* the name applied to madder roots in the Levant.

† Annales de Chimie et de Physique, tome 34, p. 228; and Journal de Pharmacie, tome 21, p. 392.

that the bones of animals which have taken for some time madder mixed with their food, are tinged red.

The colouring matter of madder has also been examined by Gaultier de Claubry and Persoz,* by H. Schlumberger,† and by Dr. F. Runge.‡ From their inquiries it is certain that alizarin is not the only or perhaps even the most important colouring matter of madder. These different inquirers have extracted various substances from madder, but do not agree in the mode of representing its constitution; as the purity however of these substances was not tested by analysis, their definite character is necessarily very doubtful. I can only enumerate here the different colouring matters extracted from madder by Dr. Runge. They are (1) *Madder purple*, dissolved out from madder, previously well washed with water between 56 and 70°, by a strong boiling solution of alum, and precipitated from the alum solution by the addition of sulphuric acid. When purified it is a light crystalline powder of a beautiful orange-yellow colour. When used in excess it imparts to cotton impregnated with the alum mordant, a deep reddish brown purple colour; but if on the contrary the cotton be in excess, the colour is bright red. (2) *Madder red*, the alizarin of Robiquet and Colin, which according to Runge may be sublimed a second time without decomposition. It may be separated from madder purple, in consequence of its insolubility in a strong solution of alum. (3) *Madder orange*, which is distinguished and separated from the two former, by its little solubility in spirits. When in excess it imparts to alumed cotton a bright orange colour. If water be added to a hot solution of it in spirit, small crystals separate, as with madder-red and madder-purple under the same circumstances. (4) *Madder yellow* is remarkable for its great solubility in water and its little affinity for cloth impregnated with alum. It abounds in Dutch madder. (5) *Madder brown*, another principle, which like the last has no value as a dye stuff.

The most fast and brilliant reds are obtained upon cotton by means of madder, as also an equally stable and valuable purple;

* Ann. de Chim. et de Phys., t. 48, 72.

† Bulletins of the Industrial Society of Mulhausen.

‡ Dr. R. D. Thomson's Records of Science, vol. 2, p. 452, and vol. 3, pp 44 and 135.

the first are known as Adrianople or Turkey reds. The colouring principles of madder have an affinity for the earth alumina and peroxides of iron and tin, like other organic colouring matters soluble in water, and form insoluble precipitates with these oxides, which are known as *lakes*. By impregnating cotton cloth with a solution of acetate of alumina, or with alum of which the acid has been in a great measure neutralised by an alkali, it retains a portion of that earth, (or of either the other metallic oxides mentioned if treated with a solution of their salts), of which it is not deprived by washing; these oxides having an attraction or affinity for the fibre of the cotton. If the cloth so prepared be introduced into a hot solution of any organic colouring matter, the latter is taken up from the solution and becomes attached to the cloth by combining with its alumina, which thus forms the link that unites the cloth and colouring matter. The alumina is termed the mordant, and such is the ordinary method of fixing colours by means of mordants. Cotton may be dyed with madder by this simple process, but the colour is dull. To produce a fine red the cloth must be submitted to a long preparation occupying some weeks, and consisting of a number of operations, the effect of many of which is very imperfectly understood, but every one of them nevertheless indispensable for a good result. The chief features of this remarkable process, without entering into a detail of the routine operations are (1) the impregnation of the cloth with an imperfect soap and some principles from sheeps' dung. By this treatment, which consists of several operations repeated more than once, the cloth acquires an animal odour, which it retains through the rest of the operations. It is said that when old cotton cloth that has been worn about the person and frequently washed is to be dyed, this process may be omitted altogether. (2) The cloth is afterwards soaked in an infusion of vegetables or of sumach, which gives it a yellow colour and assists also in fixing the madder afterwards, this is the *galling*, an accessory operation not confined to madder dyeing. (3) Alumina is fixed in the cloth in the manner previously described. (4) The cloth is then dyed by entering it into a boiler with ground or chopped madder while the water is cold, gradually raising the temperature, and boiling them together for a couple of hours. A certain quantity of bullock's blood is also added to the madder bath. The colour thus fixed is brownish red

and dull, owing to the *Madder brown* being fixed in the cloth, as well as the madder purple and madder red. The object of (5) *the clearing process* is to get rid of the brown which is not nearly so fixed as the red. It consists of boiling the cloth in alkali and soap; afterwards with soap and protochloride of tin under a pressure of two atmospheres, and finally exposing the cloth on the grass to the sun for a few days.

If the cloth be prepared and dyed with madder in the same manner, with the exception of charging it with an iron instead of an aluminous mordant, it is dyed of a beautiful and permanent purple, instead of red.*

CARTHAMIN.

Safflower consists of the flowers of *Carthamus tinctorius*; it contains two colouring matters, a yellow, which is of no value, and a beautiful but fugitive red used in silk dyeing, which is named carthamin or carthamic acid. The yellow matter is soluble in water, the red insoluble in water but soluble in alkalis. They are separated by adding an acid to an alkaline infusion of safflower, which throws down the carthamin, and afterwards passing clean cotton yarn through the liquid; in these circumstances, the yarn takes up the carthamin entirely and is then washed with water. The pure carthamin is afterwards stripped from the cotton by an alkali and the solution is employed to dye silk by acidulating with citric acid, and then passing the silk through the liquid in the usual way by means of a winch.

The pigment *rouge* contains precipitated carthamin intimately mixed with finely divided talc.

According to Doebereiner, carthamin has an acid reaction; it is but slightly soluble in alcohol or ether. Soda saturated with carthamin is said to crystallize in fine colourless needles having a silky lustre, and becoming instantly red when an acid is added.

HEMATOXYLIN.

This is the colouring matter of logwood, the wood of the *Hæmatoxylon campeachianum*; it was named *Hematin* by

* An outline of the process of Turkey red dyeing as practised at Glasgow is given by Dr. Thomson, in his *Organic Chemistry, Vegetables*, p. 396. For this and other dyeing processes, see also Leuch's *Traité complet des Matières Tincoriales*.

M. Chevreul,* who first distinguished it. It is sometimes so abundant as to exist in the wood in large crystals. The rasped or chopped wood is exhausted by means of water of a temperature between 122° and 131° , the solution evaporated to dryness by a water bath, the residue lixiviated with alcohol of 0.843 density, and the filtered solution distilled to a syrup, from which after the addition of a little water the hematoxylin is gradually deposited.

It crystallizes in reddish yellow scales, soluble in 1000 times their weight of water, dissolving easily in alcohol and ether. Acids in small quantity make it yellow, in large quantity red. The alkaline bases impart to a solution of hematoxylin a violet, purple or blue colour. Its decoction is deprived of colour by sulphuretted hydrogen (which has the same action on litmus,) and by nascent hydrogen; much of the hematoxylin probably exists in this state in the wood and acquires colour in the course of its application as a dye. Cloth impregnated with alumina is dyed *black* in a decoction of logwood, and of a fine brown in a mixture of logwood and madder. It enters into the materials for dyeing hats and broad cloth black; the effect of an acid in staining them red is due to its presence. By dry distillation hematoxylin yields ammonia, proving that it contains nitrogen.

BREZILIN.

This name has been applied by Chevreul to the colouring matter of Brazil wood, which comes to this country from Brazil and Pernambuco, and is the wood of several species of *Cæsalpina*. It is obtained by similar processes with the preceding colouring matters.

Brazilin crystallizes in orange prisms, soluble in water and alcohol. Acids give it a yellow colour; with citric acid the yellow is particularly fine. When neutralised with alkali it becomes again of a fine red, but with an excess of alkali violet or blue. In the tree it is nearly colourless, owing to the presence of free acid, and its fine red colour does not appear till all the acid which it naturally contains is saturated. This saturation is generally effected by sprinkling the ground wood with a

* Ann. de Chim. et de Phys., t. 81, p. 128.

solution of carbonate of soda, when its colour is said to be raised. A very minute quantity of alkali gives an infusion of Brazil wood a violet colour, so that it is a delicate test of alkalinity. Alum and the acetate of alumina throw down from it an abundant carmine precipitate, while the liquid retains the same colour; these compounds form the basis of common red ink. For some years past brazil-wood has been nearly superseded in this country by a wood imported from Africa, and named *camwood* by dyers, which is richer and gives a finer colour than any of the varieties of Brazil wood. It is also not so much affected by alkalies, nor so liable to assume a violet shade; and the yellow colouring matter with which it is mixed gives the red a more lively appearance (Dr. Thomson.) But the colour of these and all other red woods has little permanence and does not produce fast colours.

BERBERIN.

This is a crystalline substance of a fine yellow colour derived by the MM. Buchner from the bark of barbery root, *Berberis vulgaris*.* The root is exhausted by means of boiling water, the decoction concentrated to the consistence of a soft extract, and this digested repeatedly in alcohol of 0.844, so long as the liquid acquires a bitter taste. These tinctures are filtered, a considerable portion of alcohol distilled off, and the residue left in an open vessel to crystallize in a cool place. It forms fine prisms of a clear yellow colour, without odour, but having an intensely bitter taste. It is not fusible without decomposition. It is sparingly soluble in cold water, largely soluble in hot water, soluble in alcohol, forms compounds with bases, and precipitates readily all metallic salts. Its composition is expressed by $C_{33}H_{18}NO_{12}$. Berberin answers very well as a dye stuff, and gives a fixed yellow on cotton cloth without any mordant. It forms also a powerful tonic.

QUERCITRIN.

The yellow colouring matter of quercitron bark has lately been examined by M. Bolley.† It was obtained from a decoc-

* Journal de Pharmacie, t. 17, p. 40 and t. 21, pp. 309, 408.

† Liebig's Annalen, xxxvii, 101.

tion of the bark clarified by albumen, and having its tannin precipitated by isinglass, evaporated to an extract and treated as usual with strong alcohol. It requires about 400 parts of boiling water for solution, but dissolves in 4 or 5 parts of absolute alcohol. It is deposited in little cauliflower looking masses, which by a magnifying power of 10 times are seen to be composed of small crystals. It yields by dry distillation a yellow liquid; which soon solidifies as a clear yellow mass; this Chevreul considered as unaltered quercitrin. As it restores the colour of reddened litmus paper, and combines with and neutralises bases, M. Bolley considers it an acid and names it *Quercitronic acid*. The formula of the crystallized acid, which agrees with analysis, is $\text{HO} + \text{C}_{16}\text{H}_8\text{O}_9$, of the salt of lead $\text{PbO} + \text{C}_{16}\text{H}_8\text{O}_9$. Herm. Trommsdorff found *polychrome* to have the same composition, and represented it by the same formula halved.*

CHAPTER VIII.

ACIDS.

SECTION I.

ACIDS SUPPOSED TO CONTAIN CARBONIC OXIDE.

Carbonic acid, and chlorocarbonic acid, may be considered as combinations of carbonic oxide, as they are formed by the union of that radical with oxygen and chlorine. Carbonic oxide also unites with potassium, and by the decomposition of this compound, croconic and rhodizonic acids are produced. Oxalic and mellitic acids also appear from their composition to contain the same radical.

OXALIC ACID.

Formula of the hydrated acid, $\text{HO}, \text{C}_2\text{O}_3 + 2\text{HO}$. This acid, discovered by Scheele in 1776, exists in the form of an acid salt

* Liebig's Annalen, xiv, 205.

of potash, in a great number of plants, particularly in the species of *Oxalis* and *Rumex*; combined with lime it also forms a part of several lichens. Oxalate of lime occurs likewise as a mineral, *humboldtite*, and forms the basis of a species of urinary calculus. This acid is also produced by the oxidation of carbon in combination, in a variety of circumstances, being the general product of the oxidation of organic substances by nitric acid, hypermanganate of potash, and by fused potash. Those matters which contain oxygen and hydrogen in the proportion of water, furnish the largest quantity of oxalic acid.

This acid has been derived in quantity from lichens, but it is usually prepared by acting upon 1 part of sugar, or better, starch, by 5 parts of nitric acid, of 1.42, diluted with ten parts of water at a gentle heat till no gas is evolved, and evaporating to crystallize. The crystals must be drained, and crystallized a second time, as they are apt to retain a portion of nitric acid.

It forms long, four-sided, oblique prisms, with dihedral summits, or terminated by a single face. These crystals contain three atoms of water, one of which is basic, and the other two constitutional, or water of crystallization. The latter two may be expelled at a temperature above 212° , and the protohydrate rises at the same time in vapour, and condenses as a woolly sublimate. Heated in a retort, the hydrated acid undergoes decomposition about 311° , and is converted into carbonic oxide, carbonic acid, and formic acid, without leaving any fixed residue. Nitric acid, with heat, converts oxalic acid into water and carbonic acid. When heated with sulphuric acid, oxalic acid yields equal volumes of carbonic oxide and carbonic acid; C_2O_3 being equivalent to $CO + CO_2$, (page 308). No charring, nor evolution of any other gas occurs, so that the action of concentrated sulphuric acid affords the means of recognising oxalic acid or any oxalate. Crystallized oxalic acid is soluble in 8 parts of water, at 59° , in its own weight of boiling water, and in 4 parts of alcohol, at 59° .

Oxalates.—With potash, and with ammonia, oxalic acid forms neutral oxalates, binoxalates, and quadroxalates. Oxalate of potash, $KO, C_2O_3 + HO$, contains 1 atom of water of crystallization, which it loses a little above 212° ; it crystallizes generally in prisms of six unequal sides, terminated by oblique dihedral summits; these crystals are soluble in 3 parts of water,

insoluble in alcohol. *Binoxalate of potash*, $\text{KO}, \text{C}_2\text{O}_3 + \text{HO}, \text{C}_2\text{O}_3 + 2\text{HO}$, is sold under the name of salt of sorrel; it crystallizes in oblique, diaphanous rhomboidal prisms, which are soluble in 40 parts of cold water, 6 parts of hot water, and insoluble in alcohol. *Quadroxalate of potash*, $\text{KO}, \text{C}_2\text{O}_3 + \text{HO}, \text{C}_2\text{O}_3 + 2(\text{HO}, \text{C}_2\text{O}_3 + 2\text{HO})$, crystallizes in oblique octohedrons, of which two angles are truncated. This salt appears to be a compound of 1 atom of binoxalate of potash, with 2 atoms of hydrated oxalic acid; the 4 atoms of water of crystallization, of the last mentioned constituent escape when the salt is heated to 262° , (page 172). Oxalate of *soda*, $\text{NaO}, \text{C}_2\text{O}_3$, is the only anhydrous alkaline oxalate, and is the least soluble of the salts of soda. There is also a binoxalate of soda. The oxalates of ammonia correspond in number and composition with the salts of potash. The neutral oxalate of *ammonia*, which is formed by neutralising oxalic acid with carbonate of ammonia, is much used as a reagent, particularly to separate lime from magnesia, and generally to precipitate lime. It is less soluble than oxalic acid. When distilled in a glass retort, by a heat gradually increased, oxalate of ammonia affords a dirty white sublimate of oxamide, $\text{C}_2\text{O}_2 + \text{NH}_2$ (page 407), together with ammonia, carbonic acid, carbonic oxide, and cyanogen.

Oxalate of *lime*, $\text{CaO}, \text{C}_2\text{O}_3 + 2\text{HO}$ is thrown down as a brilliant white precipitate, remarkable for its insolubility. It is insoluble in acetic acid, but soluble in nitric and hydrochloric acids. It leaves, when heated to incipient redness by a spirit lamp, a white residue of carbonate of lime, from which the proportion of oxalic acid, or of lime, may be inferred. The oxalates of *magnesia*, *zinc*, and *manganese*, have the same composition as the oxalate of lime. The first mentioned possesses a small degree of solubility, the others are insoluble. Oxalate of *copper* forms a double salt with oxalate of ammonia, which corresponds in composition with the binoxalate of ammonia. Oxalate of *barytes* is expressed by $\text{BaO}, \text{C}_2\text{O}_3 + \text{HO}$; it is quite insoluble in water. Oxalate of *silver* is an insoluble white powder, which is anhydrous. (Phil. Trans. 1827, p. 47).

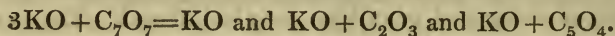
The double oxalates of *chromium*, and the aluminous class have already been described (pages 519, 566, and 611).

RHODIZONIC ACID.

Formula of the acid supposed anhydrous: C_7O_7 . Of the salt of potash, $3KO + C_7O_7$; of the salt of lead $3PbO + C_7O_7$, (Thaulow).

This body, which derives its name from the red colour of its salts, was first observed by L. Gmelin, and recognised as a new acid by Heller. Potassium, gently heated in carbonic oxide, absorbs that gas with avidity, fusing of a green tint, and spreading over the sides of the vessel; afterwards the oxycarburet becomes black and porous. Allowed to cool, it is dissolved with water, when a violent disengagement of combustible gases occurs, and a red solution is formed, containing rhodizionate of potash. The same oxycarburet of potassium is formed in large quantity, as an accidental product in the preparation of potassium from carbonate of potash and charcoal, being found as a black mass in the neck of the retort, or in the receiver with the potassium. The salt from the oxycarburet may be deprived of the excess of caustic potash by alcohol, in which the rhodizionate of potash is insoluble.

Rhodizonic acid is apt to undergo decomposition in being liberated from its salts, and has not been obtained in a state of purity. All its salts are red, and in the dry state have a metallic lustre, and reflect green. Its potash salt undergoes a remarkable decomposition when its solution is heated, being converted into free potash, oxalate of potash, and croconate of potash:



CROCONIC ACID.

Formula of the acid supposed anhydrous, C_5O_4 .

This acid derives its name from the saffron colour of its salts; it was discovered by L. Gmelin. The croconate of potash is deposited in long yellow and brilliant needles from a solution of rhodizionate of potash, which has been decomposed by ebullition. The acid may be obtained free, by decomposing croconate of potash by hydrofluosilicic acid, and evaporating to dryness. It is strongly acid, crystallizes of a yellow colour easily, and is soluble in alcohol.

Croconate of potash, $\text{KO}, \text{C}_5\text{O}_4 + 2\text{HO}$, crystallizes in long orange prisms of 6 or 8 sides, having a nitrous taste; loses its 2 atoms of water at a moderate heat and becomes lemon yellow. It is insoluble in alcohol, in common with all the salts of this acid, except the croconate of ammonia which is soluble in alcohol.

Croconate of lead, $\text{PbO}, \text{C}_5\text{O}_4 + \text{HO}$, precipitates in golden yellow micaceous plates, when a hot and dilute solution of acetate of lead is added to a solution of croconate of potash containing acetic acid.

Hydrated croconic acid has been considered as a hydracid, $\text{H} + \text{C}_5\text{O}_5$, that is, a compound of hydrogen, and a salt-radical; a constitution which is analogous, being assigned to mellitic acid.

The gas evolved when oxycarburet of potassium is dissolved in water is not pure hydrogen, but contains carbon, and is distinguished, according to Mr. E. Davy, from all the other carburets of hydrogen, by the property it possesses of inflaming at the ordinary temperature and depositing carbon, when mixed with an equal volume of chlorine.

MELLITIC ACID.

Formula of the crystallized acid: $\text{H}, \text{C}_4\text{O}_4$, or $\text{HO} + \text{C}_4\text{O}_3$ of the mellitates dried at 212° , $\text{M}, \text{C}_4\text{O}_4 + \text{HO}$, or $\text{MO}, \text{C}_4\text{O}_3 + \text{HO}$.

This acid was discovered by Klaproth in a rare mineral, *mellite*, which is the mellitate of alumina. The free acid is best obtained, according to Wöhler, by decomposing the mellitate of lead by sulphuretted hydrogen; it is a white crystalline powder, soluble in water and alcohol; from the last of which it crystallizes by slow evaporation in needles radiating from a centre. The dry acid is not altered by a temperature of 572° (300° centig.), nor is it decomposed by boiling nitric or sulphuric acid.

Mellitates.—Potash, soda and ammonia form acid besides neutral mellitates. Nitrate of potash forms a remarkable double salt with bimellitate of potash, $\text{KO}, \text{NO}_5 + 4(\text{HO}, \bar{\text{M}} + \text{KO}, \bar{\text{M}}) + 6\text{HO}$, described by Wöhler. It is remarkable that the nitrates particularly give rise to combinations in such propor-

tions. Neutral mellitate of *ammonia* undergoes a remarkable decomposition by heat, which has been lately investigated by Wöhler. Heated for some time between 302° and 320° , it loses ammonia, and is transformed into a pale yellow powder, which water decomposes into two substances, one of which, *paramide*, is white and insoluble, and the other a soluble ammoniacal salt, of which the acid is named *euchronic* (from *ευχροος*, of a fine colour). The composition of paramide is C_8HNO_4 ; it appears to be formed from 2 atoms of mellitate of ammonia, $C_8H_8N_2O_8$, by the loss of 1 atom of ammonia and 4 atoms of water. By boiling with water, particularly under pressure at 392° (200° centig.), it is converted into acid mellitate of ammonia.

Euchronic acid, $2HO, C_{12}NO_6 + 2HO$, is separated from the above acid ammoniacal salt by nitric or hydrochloric acid. It crystallizes in very small, colourless, rhomboidal prisms, which have a strong acid taste, and dissolve with difficulty; they lose $2HO$ at 392° . It fuses and is decomposed above 536° . When crystallized euchronic acid is heated to 392° , in a glass tube hermetically sealed, with a quantity of water insufficient to dissolve it, a complete solution is obtained, in which, however, the euchronic acid is converted into acid mellitate of ammonia. Euchronic acid is distinguished from all other organic compounds by the way in which it comports itself with metallic zinc. A slip of zinc dipt in a solution of this acid, immediately becomes of a magnificent blue colour at its surface; this colour becomes at the boiling point nearly as intense as that of indigo. Washed and dried, it forms a black mass which contains no zinc. When slightly heated, even upon paper, it becomes immediately completely white, and is changed anew into euchronic acid. M. Wöhler applies the name *euchroné* to the blue compound, and considers that the action of zinc in its formation is a deoxidating one, euchrone being an inferior degree of oxidation of the radical of euchronic acid, or that radical itself; but from want of material this singular and most interesting body was not fully investigated. (Ann. de Chim. &c. 3 sér. ii, 78).

Mellitate of silver undergoes a particular decomposition at 356° , losing an atom of water, and becoming Ag, C_4O_4 .

Mellitate of alumina, native mellite or honeystone is composed of $Al_2O_3, 3C_4O_4H + 18HO$, according to Wöhler. It

crystallizes in regular octohedrons, of a honey-yellow colour; is insoluble in cold water, and decomposed by boiling water.

SECTION II.

MECONIC ACID AND ITS CONGENERS.

Meconic acid, $3\text{HO}, \text{C}_{14}\text{HO}_{11} + 6\text{HO}$, is a tribasic acid, which crystallizes with 6 atoms of water of crystallization. It is found only in opium, of which it is the characteristic acid; it is named from *μηκων*, the poppy. It is best obtained by decomposing meconate of potash dissolved in 16 to 20 parts of hot water with 2 or 3 parts of pure hydrochloric acid, and crystallizes on cooling. The solutions in this process must neither be boiled, nor filtered through paper, as the latter may contain iron. (Robiquet). It crystallizes in pearly plates, which are soft to the touch, and possess an acid and astringent taste. It is sparingly soluble in cold water, but very soluble in hot water; it is equally soluble in alcohol. Salts of the peroxide of iron produce a deep red solution with meconic acid, without occasioning any precipitate. Chloride of mercury does not destroy the colour of this solution (Parnell), a property by which meconic acid may be distinguished from the persulphocyanide of iron, which is also red, but becomes yellow when chloride of mercury or gold is added to it.

A concentrated solution of meconic acid becomes yellow, when boiled, and then deep brown, and there are formed carbonic acid, oxalic acid, comenic acid, and a dark brown matter. Boiling dilute sulphuric acid, or hydrochloric acid, converts it with effervescence into carbonic acid and comenic acid.

The *meconates* contain all 3 atoms of base, one of which is generally water. Meconate of *lead* contains 2 atoms of oxide of lead; it is an insoluble white powder, which is thrown down from a solution of opium by acetate or subacetate of lead. After being washed, it is diffused through water and decomposed by a stream of sulphuretted hydrogen, to liberate the meconic acid, which may then be indicated by a persalt of iron; becoming of a wine-red colour.

Comenic acid, $2\text{HO}, \text{C}_{12}\text{H}_2\text{O}_8$, a bibasic acid, which crystallizes in very hard crusts or crystalline grains, with nothing

more than its basic water. It is formed, as already stated, on boiling a solution of meconic acid with a pretty strong acid; also by heating dry meconic acid to 392° , when carbonic acid is disengaged till the temperature rises to 446° , when the meconic acid is found to be entirely converted into comenic acid. In this transformation, the former hydrated acid loses 2 atoms of water and 2 atoms of carbonic acid: $C_{14}H_4O_{14} = C_{12}H_2O_8$ and H_2O_2 and C_2O_4 .

Comenic acid dissolves in 16 parts of boiling water; its solution decomposes the alkaline carbonates, and reddens salts of peroxide of iron. At 572° , it is decomposed and resolved into water, carbonic acid and pyromeconic acid. The comenates contain all two atoms of base, one of which is occasionally water.

Pyromeconic acid, $HO, C_{10}H_3O_5$; a monobasic acid, which presents itself as a colourless sublimate, composed of brilliant flattened plates, when crystallized comenic acid is submitted to dry distillation: $C_{12}H_4O_{10} = C_{10}H_3O_5$ and HO and C_2O_4 . Its taste is styptic, with a bitter after-taste; it fuses between 248° and 257° into an oily liquid, and sublimes without leaving any residue. It is very soluble both in water and alcohol. It reduces a solution of gold, and communicates a red colour to solutions of peroxide of iron. Its salt of *lead* is a white precipitate, of the composition, $PbO, C_{10}H_3O_5$.

SECTION III.

TANNIC ACID AND BODIES ALLIED TO IT.

The formula of tannic acid or *tannin* dried at 212° is $3HO + C_{18}H_5O_9$: it is a tribasic acid.

Tannic acid occurs in the bark of all the varieties of *Quercus* and many other trees, and in gall-nuts, from which it is procured in greatest purity. It is prepared, after Pelouze, in a percolator or apparatus of displacement, fig. 95, the lower opening of which is closed by a plug of cotton, and the vessel entirely filled with broken gall-nuts, which are more suitable for the experiment than the powder of gall-nuts. Over the gall-nuts as much aqueous ether is poured as the vessel will contain, and the mixture left to digest for several hours. The liquid is then permitted to run off into the caraffe below,

by loosening the stopper above and admitting air. It FIG. 95. is found to divide into two liquids, of which the denser syrupy and yellowish one, is a very concentrated solution of tannic acid in water, and the lighter, which is coloured green, an ethereal solution of gallic acid and other matters. Additions of ether are made to the gall-nuts, so long as two different liquids flow from the lower orifice. The aqueous ether employed is obtained by agitating common ether with water. If the gall-nuts be moistened with water before the addition of the ether, the solution of tannin which comes off is highly coloured; but if the gall-nuts be merely exposed to steam, and washed in the percolator with anhydrous ether, the process succeeds equally well as with the aqueous ether.



By the evaporation of the solution of tannin, a yellow light mass is generally obtained, which is purified by solution in water, and evaporation in vacuo over sulphuric acid. It then forms a mass colourless or slightly yellow, which is not crystalline but resembles dried gum, and becomes somewhat deeper in tint in humid air, but is not otherwise altered. It is dissolved easily by water and in large quantity; the taste of the solution is purely astringent without bitterness, it reddens vegetable blues, and decomposes alkaline carbonates with effervescence. Tannic acid is soluble in aqueous alcohol, but only very slightly soluble in ether. Its solution is affected by air, particularly at a high temperature, oxygen being absorbed and an equal volume of carbonic acid evolved, while the tannic acid is transformed into gallic and ellagic acids. But the solution of tannic acid keeps without change in close vessels. A moderately strong solution of tannic acid gives with sulphuric, hydrochloric, phosphoric, arsenic or boracic acid, a thick white precipitate, which is a compound of the two acids mixed, and is very soluble in pure water and in alcohol. When the solution of tannic acid is precipitated hot by sulphuric acid, a resinous mass is formed, which dissolves in dilute sulphuric acid at the point of ebullition, of a deep tint, and after being boiled for some minutes is converted, without any evolution, of gas, into gallic acid, which crystallizes on the cooling of the solution.

Tannic acid boiled in an excess of caustic alkali, undergoes the same transformation.

Tannic acid precipitates animal gelatine entirely from solution in thick flocks, which adhere and form a viscid elastic mass when the acid is in excess; this precipitate dissolves in the supernatant liquid at the boiling point. It is known as *tannogelatin*, and contains about half its weight of tannin. Tannin is also absorbed from solution by the fresh skin of animals, which is then tanned or converted into leather, and ceases to be soluble in water or to be putrescible. Tannic acid also precipitates a solution of starch and of albumen, and is capable of combining with animal fibrin.

Tannates.—The neutral tannate of potash or ammonia appears as a thick precipitate, when a moderately dilute solution of tannic acid is treated with that alkali or its carbonate; the precipitate is very soluble in an excess of alkali. Tannates of barytes, strontian, lime, and magnesia are very sparingly soluble. Salts of protoxide of iron undergo no alteration when mixed with a solution of tannic acid, but if exposed to air become soon of a deep bluish black colour. Tannate of *peroxide of iron* is a black pulverulent precipitate, $\text{Fe}_2\text{O}_3, \text{C}_{18}\text{H}_5\text{O}_9 + 9\text{HO}$ (Pelouze), formed on adding persulphate of iron to a solution of tannic acid; it is the basis of writing ink. A good black ink is prepared from bruised Aleppo galls 6 ounces, copperas (sulphate of iron) 4 ounces, gum arabic 4 ounces, water 6 pints. The galls are boiled in the water, the other ingredients then added, and the whole kept in a wooden or glass vessel and occasionally shaken. In two months strain, and pour off the ink into glass bottles to be well corked. To prevent mould, add one grain of corrosive sublimate or three drops of creosote to each pint of ink. (Brande's Manual, p. 1105). Tartar emetic gives a white precipitate with tannic acid, the tannate of *antimony*, $\text{HO}_3 + 3\text{C}_{18}\text{H}_5\text{O}_9$. Tannic acid forms sparingly soluble white precipitates with most of the organic bases.

GALLIC ACID.

Formula of the crystallized acid, $2\text{HO}, \text{C}_7\text{HO}_3 + \text{HO}$; of the acid dried at 212° ; $2\text{HO}, \text{C}_7\text{HO}_3$. Of one gallate of lead dried

at 212° : $\text{HO}, \text{PbO} \cdot 2\text{C}_7\text{HO}_3 + \text{HO}$; the last atom of water is lost at 320° . Of another gallate of lead: $2\text{PbO}, \text{C}_7\text{HO}_3$. Of acid gallate of ammonia, the composition is expressed by $\text{NH}_4\text{O}, \text{C}_7\text{HO}_3 + 2\text{HO}, \text{C}_7\text{HO}_3$; it loses nothing at 212° . These are the only salts of gallic acid of which the composition is certainly known, and they are not sufficient to determine whether or not gallic acid is bibasic.

The metamorphosis of tannic acid into gallic acid, under the influence of boiling dilute sulphuric acid has already been adverted to. The same change occurs in an aqueous extract of gallnuts exposed to air for several months. By the absorption of 8 atoms of oxygen, 1 atom of hydrated tannic acid might be converted into 2 atoms of hydrated gallic acid, 4 atoms of carbonic acid, and 2 atoms of water: $\text{C}_{18}\text{H}_8\text{O}_{12}$ and $\text{O}_8 = 2\text{C}_7\text{H}_3\text{O}_5$ and 4CO_2 and 2 HO. Much ellagic acid is also formed in the transformation of the tannin of gallnuts, in the air. To prepare gallic acid, a strong extract of gallnuts in cold water may be precipitated in the cold by sulphuric acid; the thick mass be mixed with dilute sulphuric acid, expressed while still humid, and introduced in this state into a mixture of sulphuric acid with two parts of water at the boiling temperature. The liquid is boiled for some minutes and then allowed to cool; crystals of gallic acid are deposited, which may be purified by crystallizing again from water, converting the new product, which is still coloured, by means of acetate of lead into an insoluble gallate of lead, which last is washed, then diffused through water, and decomposed by a stream of sulphuretted hydrogen gas; the sulphuret of lead, which is then formed, assists in carrying down the colouring matter.

Gallic acid crystallizes on cooling from a hot solution, in thin, silky needles. It requires 100 parts of cold water to dissolve it, but is soluble in 3 parts of boiling water. It is also very soluble in alcohol, and to a small extent in ether. When pure it does not precipitate a solution of gelatine. The aqueous solution of this acid may be kept apart from air without change, but with access of oxygen it undergoes decomposition, a brown matter being deposited, while carbonic acid is evolved and the surface becomes covered with mouldiness. This decomposition is greatly promoted by the presence of a mineral acid, or of an alkali in the solution. With salts of peroxide of iron gallic

acid assumes a deep blue tint; the black precipitate which falls, left in contact with gallic acid, is gradually reduced to the state of protoxide, but not when a salt of the ferrosoferric oxide has been employed in its formation.

When crystallized gallic acid is dissolved in concentrated sulphuric acid, and the solution heated, it assumes a crimson tint at a temperature above 284° . If allowed to cool in this state, and cold water afterwards added, an abundant precipitate is formed of a reddish brown colour and crystalline aspect, which appears to be gallic acid that has lost an atom of water, its composition after drying being $C_7H_2O_4$ (Robiquet). It is insoluble in water, but dissolves easily in alkalies, and has some analogy, according to Robiquet, to the colouring matter of madder. It is decomposed by dry distillation, giving small cinnabar-red prismatic crystals.

All the *gallates* are remarkable for the facility with which they absorb oxygen, when in contact with an excess of alkali; carbonic acid is then formed and a brown matter insoluble in water. In a mineral water alkaline from the presence of lime or magnesia, an addition of gallic acid causes the liquid gradually to become turbid from the formation of a black precipitate, although no iron be present, owing to the decomposition of the gallic acid itself.

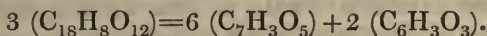
Pyrogallic acid, $C_6H_3O_3$, or $C_8H_4O_4$ (the equivalent being doubtful), is prepared by heating briskly either tannic or gallic acid, previously well dried, in a retort by means of a spirit-lamp till coloured empyreumatic products come over. The pyrogallic acid is obtained as a crystalline sublimate, which may be purified by a second sublimation at a gentle heat. It forms white plates or needles, fuses at 239° , boils at 410° , and sublimes without alteration. It does not redden litmus; its taste is bitter and slightly astringent. It dissolves in $2\frac{1}{4}$ parts of water at 55.4 (13° centig.); the solution absorbs oxygen and deposits a brown powder. It is equally soluble in alcohol and ether. When heated briskly above 482° (250° centig.), pyrogallic acid blackens, and is converted into water and metagallic acid.

Pyrogallate of lead, a white precipitate formed on adding a solution of pyrogallic acid to acetate of lead, is $PbO, C_6H_6O_3$,

according to Berzelius, and also Pelouze, but $\text{PbO}, \text{C}_8\text{H}_8\text{O}_4$ according to the later analysis of R. C. Campbell.

Metagallic acid, melangallic acid (Berzelius). The formula of the anhydrous acid is $\text{C}_6\text{H}_2\text{O}_2$ (Pelouze); its probable atomic weight: $\text{HO}, \text{C}_{12}\text{H}_3\text{O}_3$. This body remains as a fixed residue in the retort when gallic acid or tannic acid is heated by an oil bath to 482° , till all the volatile products escape. It is then dissolved in a solution of alkali and precipitated by an acid to obtain it in a state of purity. It is a black powder, insoluble in water, which forms soluble compounds with alkalies of a deep black colour.

Tannic and gallic acids, although differing so much in composition, afford the same products when decomposed by heat. This is explained by supposing tannic acid a compound of gallic and pyrogallic acids. In fact 3 atoms of tannic acid contain the elements of 6 atoms of gallic acid, and 2 atoms of pyrogallic acid.



Ellagic acid.—The gallic acid which forms in an infusion of gallnuts exposed to air, is always accompanied by a grey powder, which being insoluble, may be purified by boiling water; it is the acid in question. Ellagic acid dissolves in alkalies and is precipitated by acids. According to Pelouze it possesses the same composition as dried gallic acid, $\text{C}_7\text{H}_3\text{O}_5$; between 212° and 248° , it loses an atom of water and becomes $\text{C}_7\text{H}_2\text{O}_4$.

Catechu, the brown dried extract of the *Acacia* or *Mimosa catechu* contains a large quantity of tannic acid differing little from the tannic acid of gallnuts, which may be extracted by cold water. The portion insoluble in cold water, contains a particular principle *catechin*, $\text{C}_{15}\text{H}_6\text{O}_6$ (Swanberg). Two acids are produced when catechin with alkalies or alkaline carbonates absorbs oxygen from the air, and forms black solutions with the former and red with the latter; which have been named *japonic acid*, $\text{HO} + \text{C}_{12}\text{H}_4\text{O}_4$, and *rubinic acid*, $\text{HO}, \text{C}_{18}\text{H}_6\text{O}_9$ (Swanberg.)

SECTION IV.

CITRIC ACID AND THE PRODUCTS OF ITS DECOMPOSITION.

Formula of citrate of silver, $3\text{AgO} + \text{C}_{12}\text{H}_5\text{O}_{11}$. Of the crystals of citric acid formed on the cooling of a solution saturated at 212° , $3\text{HO}, \text{C}_{12}\text{H}_5\text{O}_{11} + \text{HO}$, which may be named hydrate A; this hydrate loses no weight and preserves its transparency at 212° . It is the type upon which most of the citrates are formed. Of the crystals formed by the spontaneous evaporation of a solution saturated in the cold, the formula is $3\text{HO}, \text{C}_{12}\text{H}_5\text{O}_{11} + 2\text{HO}$; of which the two atoms of water of crystallization are lost at 212° .

Citric acid was discovered by Scheele; it exists in a considerable variety of plants, but is procured only in quantity from the orange and lemon and from gooseberries. The acid juice of these fruits is neutralised by a known weight of carbonate of lime; the insoluble citrate of lime washed, and then decomposed by a quantity of oil of vitriol equal in weight to the carbonate of lime used, diluted with 5 parts of water. The acid liquid is separated by filtration, from the insoluble sulphate of lime; and the citric acid crystallized with a slight excess of sulphuric acid present, which is observed to favour the crystallization, while it is impeded by citrate of lime in solution.

Citric acid crystallizes in regular rhomboidal prisms, terminated by four faces, has an agreeable acid taste, and is soluble in an equal weight of water forming a thick syrup. A dilute solution of citric acid in water does not keep, but becomes covered with mouldiness. When pure, citric acid dissolves completely in alcohol, without residue, and does not give a precipitate with lime-water. But when a few drops of the acid are added to the latter in excess, the clear liquid obtained becomes turbid when heated, from the deposition of a white basic citrate of lime, $3\text{CaO}, \text{C}_{12}\text{H}_5\text{O}_{11} + \text{CaO}, \text{HO}$, which dissolves in acids without effervescence. Citric acid is commonly distinguished by that property. Hydrate A of citric acid, which contains 4 atoms of water fuses at 266° , and loses nothing, although hydrate B, which contains 5HO, loses 2HO at 212° . When the temperature of 302° is exceeded the acid of both hydrates undergoes decomposition. When 1 part of

crystallized citric acid is gently heated with 4 parts of oil of vitriol, a considerable quantity of carbonic oxide is evolved, and acetic acid is formed. When fused with an excess of hydrate of potash, citric acid is decomposed into oxalic and acetic acids; 1 atom of citric acid containing the elements of 2 atoms of acetic acid, 2 atoms of oxalic acid and 2 atoms of water.

Citrates.—The neutral salts of citric acid, besides 3 atoms of fixed base, carry along with them the atom of water of acid hydrate A; which water however they either abandon at the ordinary temperature, like the citrate of silver, or at a high temperature. In certain subcitrates this atom of water is replaced by an atom of metallic oxide, such as lime or oxide of lead. The composition of these salts has received considerable attention. The following are the formulæ of the most remarkable citrates:

Citrates of *potash*: three salts exist containing as base respectively, 3KO ; $2\text{KO} + \text{HO}$; and $\text{KO} + 2\text{HO}$. Citrates of *soda*: salt A, $3\text{NaO}, \text{C}_{12}\text{H}_5\text{O}_{11} + 11\text{HO}$ (Berzelius); loses 7HO at 212° , and the remaining 4HO between 374° and 392° (190° and 200° centig.). Salt B, $2\text{NaO}.\text{HO}, \text{C}_{12}\text{H}_5\text{O}_{11}$. Salt C, $\text{NaO}.2\text{HO}, \text{C}_{12}\text{H}_5\text{O}_{11}$. Citrate of *barytes*, $3\text{BaO}, \text{C}_{12}\text{H}_5\text{O}_{11} + 7\text{HO}$ (Berzelius); loses 6HO at 302° and becomes anhydrous at 374° . Another citrate of barytes appears to be a compound of the preceding salt, with $2\text{BaO}.\text{HO}, \text{C}_{12}\text{H}_5\text{O}_{11}$, its empirical formula being $2\text{C}_{12}\text{H}_5\text{O}_{11} + 5\text{BaO} + 8\text{HO}$. Citrate of *lime*, $3\text{CaO}, \text{C}_{12}\text{H}_5\text{O}_{11} + 4\text{HO}$ (Berzelius); it loses 3HO at 212° , and the remaining HO at a higher temperature. The subcitrate of lime lately mentioned loses HO at 212° . Citrates of *lead*: salt A, $3\text{PbO}, \text{C}_{12}\text{H}_5\text{O}_{11} + \text{HO}$. Salt B, $2\text{PbO}.\text{HO}, \text{C}_{12}\text{H}_5\text{O}_{11} + 2\text{HO}$. Salt C, $3\text{PbO}, \text{C}_{12}\text{H}_5\text{O}_{11} + 3\text{PbO}$. Salt D, $3\text{PbO}, \text{C}_{12}\text{H}_5\text{O}_{11} + \text{PbO}, \text{HO}$. Citrate of *copper*, $3\text{CaO}, \text{C}_{12}\text{H}_5\text{O}_{11} + \text{CaO}$. Citrate of *silver*, $3\text{AgO}, \text{C}_{12}\text{H}_5\text{O}_{11} + \text{HO}$; loses HO between 68° and 77° . Citrate of *antimony* and *potash*, $\text{SbO}_3, \text{C}_{12}\text{H}_5\text{O}_{11} + 3\text{KO}, \text{C}_{12}\text{H}_5\text{O}_{11} + 5\text{HO}$ (Thaulow); it crystallizes in prisms of a brilliant whiteness which lose their whole water of crystallization at 212° . Citrate of *ethyl* $3\text{EO}, \text{C}_{12}\text{H}_5\text{O}_{11}$. (Liebig's Traité, ii, 45.)

Aconitic acid, $\text{HO} + \text{C}_4\text{H}_2\text{O}_3$.—When crystallized citric acid is heated, it fuses, gives off water, but undergoes no essential change till inflammable gases are disengaged, and afterwards an

acid liquid which condenses in oily striæ, with carbonic acid gas. These appearances indicate two stages in the distillation, and if the process be interrupted when the disengagement of water and inflammable vapour ceases, the fixed residue in the retort contains no citric acid, but a new acid produced by its decomposition, which proves to be the same with the acid from the *Aconitum napellus* and *Equisetum fluviatile*, and which was already known under the names of aconitic and equisetetic acid. This acid is soluble in ether, which citric acid is not. It is also readily converted into aconitic ether, by the action of dry hydrochloric acid upon its solution in alcohol, and is precipitated by water, while citric acid not being etherified by this process remains in the liquor. Aconitic ether is easily decomposed by caustic potash, and the acid may be derived from the potash salt. Aconitic acid forms only small confused crystals. When briskly distilled it affords the two following isomeric acids, which sublime (see page 712.)

Itaconic acid, $\text{HO} + \text{C}_5\text{H}_2\text{O}_3$; known also as pyrocitric acid and citricic acid. It crystallizes in rhomboidal tables, is soluble in 17 parts of water at 50° , in 10 at 68° ; soluble also in alcohol and ether.

Citraconic acid (hydrated), $\text{HO} + \text{C}_5\text{H}_2\text{O}_3$; distinguished also as citribic acid by M. Baup. It is obtained anhydrous by distillation as an oily limpid liquid, $\text{C}_5\text{H}_2\text{O}_3$, which distils at 212° without decomposition.

SECTION V.

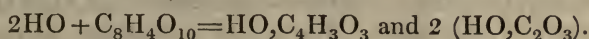
TARTARIC AND PARATARTARIC ACIDS AND THE PRODUCTS OF THEIR DECOMPOSITION.

TARTARIC ACID.

Formula of the crystallized acid, $2\text{HO} + \text{C}_8\text{H}_4\text{O}_{10}$; a bibasic acid.

This acid, which in common with so many others was first prepared by Scheele, exists in many fruits, and also as tartrate of lime in several roots, but is prepared only from the juice of the grape, which contains tartaric acid in the form of tartar or bitartrate of potash. The last salt precipitates during the fermentation of wine, owing to its insolubility in alcohol; in the crude state, it is known as *argol*, and is highly coloured, when

purified, as cream of tartar. To procure tartaric acid, cream of tartar is dissolved in boiling water and neutralised with carbonate of lime, which throws down one half of the tartaric acid as an insoluble tartrate of lime; the other half of the acid contained in the neutral tartrate of potash, is precipitated by a solution of chloride of calcium. The tartrate of lime is decomposed by an equivalent quantity of sulphuric acid, and the tartaric acid separated from the insoluble sulphate of lime by filtration; 3 parts of oil of vitriol are usually taken for 5 parts of cream of tartar. The acid solution is evaporated in leaden vessels by a gentle heat, during which process some sulphate of lime is deposited. A syrupy solution of tartaric acid left in a warm place yields crystals which are oblique prisms of a rhombic base, terminated by dihedral summits and truncated on the longitudinal edges, or hexagonal prisms terminated by three faces of truncation; but the two parallel faces are generally more developed than the others, so as to give the crystals the appearance of tables. The crystals are persistent in air, of a strongly acid and agreeable taste, dissolve in $1\frac{1}{2}$ parts of cold water and in less hot water, and are equally soluble in alcohol. The aqueous solution of tartaric acid and its salts undergoes decomposition, and becomes covered with mouldiness. When the crystallized acid is heated, it loses water and produces a series of new compounds. Treated at a high temperature with a strong solution of hydrate of potash, tartaric acid is entirely converted into acetate and oxalate of potash; one atom of crystallized tartaric acid actually containing the elements of 1 atom of hydrated acetic acid and two atoms of hydrated oxalic acid:



A solution of tartaric acid does not disturb solutions of chloride of barium and chloride of calcium, but produces a white precipitate in barytes and lime-water, and in acetate of lead. A solution of tartaric acid is also used in precipitating potash from its salts, when not very dilute, the bitartrate of potash falling down, upon agitation, as a granular precipitate, which is sparingly soluble in water, but dissolves readily in hydrochloric acid. The addition of tartaric acid to many metallic solutions, prevents their precipitation by alkalies.

Tartrates.—According as one or both atoms of water in tar-

taric acid are replaced by a metallic oxide, an acid or neutral tartrate is formed, and when the 2 atoms of metallic oxide are different, a double tartrate.

Neutral tartrate of *potash*, $2\text{KO}, \text{C}_8\text{H}_4\text{O}_{10}$ is anhydrous, and soluble in an equal weight of cold water. Acid tartrate of potash (bitartrate), $\text{HO.KO}, \text{C}_8\text{H}_4\text{O}_{10}$ is also anhydrous, soluble in 18 parts of boiling water, and in 184 parts of water at 68° ; it is insoluble in alcohol. Purified tartar, when heated alone, gives a carbonaceous mixture (*black flux*), and when deflagrated with 2 parts of nitre, it leaves white carbonate of potash (*white flux*). Tartrate of *potash* and *soda*, or rochelle salt, $\text{KO.NaO}, \text{C}_8\text{H}_4\text{O}_{10} + 10\text{HO}$ (Schulze), is formed by neutralising acid tartrate of potash with carbonate of soda, is soluble in half its weight of cold water and persistent in air. It crystallizes with two equivalents of the tartrate of potash and boracic acid, and forms a double salt, which is anhydrous. Neutral tartrate of *ammonia*, $2\text{NH}_4\text{O}, \text{C}_8\text{H}_4\text{O}_{10} + 2\text{HO}$ (Dulk). Acid tartrate of ammonia resembles acid tartrate of potash. A hot solution of this salt dissolves a large quantity of *arsenious acid*, and yields, by evaporation, large and transparent crystals of a salt of two bases, $\text{NH}_4\text{O.AsO}_3, \text{C}_8\text{H}_4\text{O}_{10}$, analogous in composition to tartrate of potash and antimony. Tartrate of *potash* and *boracic acid*, $\text{KO.BO}_3, \text{C}_8\text{H}_4\text{O}_{10}$ (Duflos), is a white uncrystalline mass, very soluble in water, obtained by dissolving a mixture of $47\frac{1}{2}$ parts of cream of tartar (1 atom), and $15\frac{1}{2}$ parts of crystallized boracic acid (1 atom), by means of hot water. Heated in a dry condition to 482° (250° centig.), this salt loses 2HO , like tartrate of antimony and potash, at the expense of the elements of the acid, the empirical formula of the salt becoming $\text{C}_8\text{H}_2\text{O}_8, \text{KO}, \text{BO}_3$ (Soubeiran and Capitaine). Tartrate of *potash* and *peroxide of iron* is a pharmaceutical preparation; its composition when dried at 212° is $\text{KO.Fe}_2\text{O}_3, \text{C}_8\text{H}_4\text{O}_{10}$, (S. and C.). Tartrate of *antimony* is a salt, crystallizing with difficulty, of which the composition is unknown. Three double tartrates of *antimony* and *potash* are known: (1) Tartar emetic (page 639,) the formula of which, dried at 212° , is $\text{KO.SbO}_3, \text{C}_8\text{H}_4\text{O}_{10}$, and heated to 392° (200° centig.), $\text{KO.SbO}_3, \text{C}_8\text{H}_2\text{O}_8$. (2.) Tartar emetic combines with 3 atoms of the acid tartrate of potash, and forms a crystallizable double salt, when the mixture of these two salts is kept constantly boiling in the preparation of tartar emetic

(Knapp). (3). A salt $\text{KO.SbO}_3, 2\text{C}_8\text{H}_4\text{O}_{10} + 7\text{HO}$ (Knapp), formed by dissolving together 9 parts of tartar emetic, and 4 parts of crystallized tartaric acid, which is very soluble and crystallizable. Tartrate of *antimony* and *lead*, $\text{PbO.SbO}_3, \text{C}_8\text{H}_4\text{O}_{10}$ (Dumas), the white precipitate which falls on adding a salt of lead to a solution of tartar emetic, dried at 212° . Heated to 392° , it loses 2HO , like tartar emetic.

Action of heat upon tartaric acid.—Tartaric acid fuses between 266° and 284° , and becomes brown at 320° . By the action of heat it loses first one fourth, then one half, and finally the whole of the water of its hydrate (Fremy), forming two new acids, the relation of which to tartaric will be best seen by doubling the formula of the latter :

Anhydrous tartaric acid . . .	$\text{C}_{16}\text{H}_8\text{O}_{20}$
Tartrelic acid	$\text{C}_{16}\text{H}_8\text{O}_{20} + 2\text{HO}$
Tartralic acid	$\text{C}_{16}\text{H}_8\text{O}_{20} + 3\text{HO}$
Crystallized tartaric acid . .	$\text{C}_{16}\text{H}_8\text{O}_{20} + 4\text{HO}$

When the solutions of the modified acids are boiled, they are quickly converted into ordinary tartaric acid.* Representing anhydrous tartaric acid by $\text{C}_4\text{H}_2\text{O}_5$, we have then, for the modified acids, the following formulæ (Liebig) :

$2(\text{C}_4\text{H}_2\text{O}_5) + 2\text{HO}$. .	crystallized tartaric acid.
$3(\text{C}_4\text{H}_2\text{O}_5) + 2\text{HO}$. .	tartralic acid.
$4(\text{C}_4\text{H}_2\text{O}_5) + 2\text{HO}$. .	tartrelic acid.

The salts of tartralic and tartrelic acids with alkaline bases are not crystallizable. Anhydrous tartaric acid is produced by keeping the crystallized tartaric acid for some time in an oil bath, at 302° (150° centig.) ; it is insoluble in cold water.

Tartaric acid yields the two following acids by its destructive distillation :

Liquid pyrotartaric acid, $\text{HO.C}_6\text{H}_3\text{O}_5$, which forms a mono-basic ether and other salts.

Solid pyrotartralic acid, $\text{HO.C}_5\text{H}_3\text{O}_3$ (Pelouze), is formed only in small quantity by the distillation of tartaric acid, but in

* Fremy ; Ann. de Chim. et de Phys. t. 68, p. 353.

larger quantity by the distillation of acid tartrate of potash (Weniseles).

PARATARTARIC (RACEMIC) ACID.

Liebig assigns to this acid, dried at 212° , the formula $\text{HO} + \text{C}_4\text{H}_2\text{O}_5$, which contains half the number of atoms in tartaric acid, and considers the former as a monobasic acid, while tartaric acid is bibasic. By this difference, the isomerism of these two acids (page 157) is accounted for. Crystallized paratartaric acid contains an additional atom of water, and is represented by $\text{HO}, \text{C}_4\text{H}_2\text{O}_5 + \text{HO}$.

Paratartaric acid was discovered by Mr. Kestner, of Thann, and particularly studied by John, by Gay-Lussac and Berzelius. It forms no double salt of potash and soda, analogous to Rochelle salt, and is probably on that account monobasic. Paratartaric acid is contained in the cream of tartar of the wines of the Vosges, and perhaps other localities, and is separated by neutralising that salt with carbonate of soda, and crystallizing out the tartrate of potash and soda. The mother liquor is precipitated by chloride of calcium, and the mixed tartrate and paratartrate of lime decomposed by sulphuric acid; on concentrating, the paratartaric acid crystallizes before the tartaric, being considerably less soluble.

Paratartaric acid crystallizes in oblique prisms, of a rhombic base, which effloresce in dry air. It is a more powerful acid than tartaric, decomposing nitrate and sulphate of lime and chloride of calcium, with precipitation of paratartrate of lime. Hence paratartaric acid was first mistaken for oxalic acid. The paratartrate of lime so formed, dissolves in hydrochloric acid, and is precipitated by ammonia.

Paratartrates.—These salts are identical in composition with the tartrates of the same base, but only a few of them have been examined. Paratartrate of *lead* is an insoluble white powder. Paratartrate of *antimony* and *potash* is prepared in the same way as tartar emetic, and has the same composition, but differs in crystalline form, being in four-sided prisms, of a rhombic base, or in needles grouped about a centre. Paratartaric acid has little disposition to form double salts.

According to the observations of Fremy, crystallized para-

tartaric acid loses water when heated, and gives rise to two new and peculiar acids, corresponding in composition with tartralic and tartrelic acids. At a still higher temperature, it gives rise to a body which is identical in properties with anhydrous tartaric acid. It gives also by dry distillation the same two pyrogen acids as tartaric acid.

SECTION VI.

MALIC ACID.

Formula of the hydrated acid ; $2\text{HO} + \text{C}_8\text{H}_4\text{O}_3$. Malic acid is bibasic (Hagen).

This is the acid of apples, from which it derives its name, but is of frequent occurrence in other acidulous fruits and vegetable juices, where it is accompanied by citric and tartaric acids. It is generally prepared from the berries of the mountain ash (*Sorbus acuparia*). The fruit is collected in August, while scarcely red and before it is ripe. It is bruised in an iron mortar, the juice expressed, filtered through linen, and treated in a bason of copper with a thin milk of lime till the mixture commences to change colour. An excess of lime occasions a deep green coloration, but the liquid ought to have a slight acid reaction, and to retain a reddish brown colour. When now made to boil, a large quantity of a neutral malate of lime precipitates, crystalline and granular, which may be taken out as it collects, by means of a colander. After this is deposited, a new portion of milk of lime may be added, with the same precautions, and a fresh portion of malate of lime is obtained. This salt is washed cold, and introduced while still humid into a boiling mixture of 1 part of nitric acid and 10 parts of water, so as to dissolve it. A concentrated solution deposits on cooling a large crop of colourless and regular crystals, of the acid malate of lime. The addition of acetate of lead to the purified acid malate of lime, throws down a curdy white precipitate, which contains lime, but on allowing it to digest at a moderate heat in an excess of acetate of lead, the lime is abandoned, and crystals form in four-sided prismatic needles, grouped about a common centre, and possessing a silky lustre, which are neutral malate of lead, containing 6 atoms of water of crystallization.

The acid is now obtained by decomposing the malate of lead diffused through water, by a stream of sulphuretted hydrogen, the sulphuret of lead separated by filtration, and the liquid evaporated, first by the naked fire, and afterwards by a water-bath, to the consistence of a syrup. (Liebig).

The hydrated acid forms granular crusts, of which the crystallization is confused, and which are deliquescent. Its solution is very acid; it reduces the salts of gold; the dry acid dissolves entirely in alcohol. The crystallized acid fuses at 266° or 284° (130° or 140° centig.), but when kept for some time at that temperature, crystalline plates form in it, and gradually increase in quantity; these are *fumaric acid*, which is sparingly soluble in cold water. By dry distillation, malic acid affords water and afterwards a volatile and crystallizable acid, named maleic acid by Pelouze.

Malates.—Malic acid forms both neutral and acid salts with the alkaline and magnesian bases, the second atom of water in the acid salts being water. The malate of peroxide of iron is the only one which dissolves in alcohol.*

Maleic acid (hydrated), $2\text{HO} + \text{C}_8\text{H}_2\text{O}_3$. This acid comes over on the brisk distillation of malic acid. It crystallizes in plates or in oblique prisms of a rhombic base, is very soluble in water, alcohol and ether, its taste is acid and disagreeable. Distilled by a sharp heat it is decomposed, and resolved into water and a white volatile matter, *anhydrous maleic acid*, fusible at $134^{\circ}.6$, and boiling at 349° . There exist both a neutral and acid maleate of *silver*, the first containing 2 atoms of oxide of silver, and the last, 1 atom of oxide of silver with 1 atom of water as base, so that maleic acid is certainly bibasic.

Fumaric acid, $\text{HO} + \text{C}_4\text{HO}_3$; a monobasic acid, produced by heating malic acid, and also existing in fumitory (*Fumaria officinalis*), and in Iceland moss. The same acid is formed when the malates of an alkaline base are exposed to a high temperature. Fumaric acid thus appears to be related to malic acid, as pyrophosphoric acid is to phosphoric acid; but Dr. Hagen did not succeed in transforming fumaric acid again into malic, by boiling a solution of the former. Fumaric acid crystallizes

* Dr. Hagen on Malic Acid; Memoirs of the Chemical Society of London, vol. i, p. 28.

in fine micaceous plates, soluble in 200 parts of cold water; it is more soluble in hot water and also in alcohol. It crystallizes from boiling nitric acid without change. Fumaric acid may be sublimed from a spatula, in the open air, without leaving any residue, but is decomposed in a great measure when distilled in a retort. A volatile *fumaric ether* was formed by Hagen; and by digesting the latter with aqueous ammonia, *fumaramide*, $C_4HO_2 + NH_2$, which is an amorphous powder, of brilliant whiteness, almost insoluble in cold water and in alcohol.

SECTION VII.

KINIC OR QUINIC ACID.

The formula of neutral kinate of silver is $AgO + C_{14}H_{11}O_{11}$; of neutral kinate of lime, $CaO + C_{14}H_{11}O_{11}$, from which it is inferred that the formula of anhydrous kinic acid is $C_{14}H_{11}O_{11}$. The formula of the crystallized acid is $C_7H_6O_6$, or $C_{14}H_{12}O_{12} = HO + C_{14}H_{11}O_{11}$. But the kinates of lead and copper appear to belong to another class, of which the acid is bibasic, and its hydrate $2HO + C_7H_4O_4$; the formula of the kinate of lead being $2PbO + C_7H_4O_4$, and the formula of the basic kinate of copper, $CuO.HO + C_7H_4O_4$ (Woskresensky).

Kinic acid was discovered, in 1790, by Hoffmann. It exists as kinate of lime in the bark of all the quinquinas, and according to Berzelius, accompanies gallic acid in the laburnum of many trees. In preparing quinine and cinchonine, by boiling the bark of quinquina with hydrochloric or sulphuric acid, and precipitating the alkali from the extract by an excess of lime, the kinate of lime remains dissolved, and is deposited from the solution evaporated to a syrupy consistence, in the state of crystals. The salt is decomposed by heating gently for several hours a mixture of $6\frac{1}{2}$ parts of it, with 1 part of concentrated sulphuric acid diluted with 10 parts of water. The supernatant liquid is drawn off from the precipitated sulphate of lime, alcohol added to it so as to throw down the sulphate of lime remaining in solution; and finally, the clear solution is evaporated by a moderate heat to a syrupy consistence, and left to itself. The kinic acid crystallizes in voluminous crystals derived from a

prism of rhombic base, greatly resembling tartaric acid; they are persistent in air. (Liebig's *Traité*, ii, 122).

Kinic acid is soluble in 2 parts of boiling water; it is also soluble in alcohol. By dry distillation it yields a volatile crystalline acid, of which little is known. Kinic and gallic acids appear to be related; indeed gallic acid, which is $C_7H_3O_5$, may be considered as a kinic acid $C_7H_4O_4$, in which 1 equivalent of hydrogen is replaced by 1 equivalent of oxygen (Liebig).

Kinates.—All the kinates are soluble in water, with the exception of the kinate of lead containing 2 atoms of oxide of lead; alcohol precipitates them from their aqueous solutions.

Kinoïle is a product of the calcination of a kinate by a gentle heat, and of the action of peroxide of manganese and sulphuric acid upon crystallized kinic acid. It is a remarkable neutral substance, of a golden yellow colour and high lustre, heavier than water, fusing and volatilising without decomposition at 212° (Woskresensky).

SECTION VIII.

VOLATILE ACIDS OF BUTTER.

Butyric acid, $HO, C_8H_{15}O_3$ (Chevreul). This is an oily limpid liquid, having the odour of rancid butter and a nauseous and ethereal taste. Its density is 0.9765 at 77° ; it evaporates easily in the open air, and boils above 212° . By distillation butyric acid gives *butyrone*, C_6H_6O (Kraus), the formula of butyric acid being supposed $C_7H_6O_3$ (Loewig).

Caproic acid, $HO + C_{12}H_{23}O_3$ (Chevreul), is an oily limpid liquid, having the odour of sweat and a nauseous taste, with a sweetish after-taste of apples. Its density is 0.922 at 71.8° , it evaporates in open air, boils above 212° , is soluble in 96 parts of water at $44^\circ.6$. It is miscible with alcohol, ether and oils.

Capric acid, $HO + C_{18}H_{35}O_3$ (Chevreul), when liquid, greatly resembles caproic acid in physical properties. When agitated at $52^\circ.7$ it forms a mass of fine needles, which become entirely liquid at $64^\circ.4$. It has the same odour as caproic acid, with that also of the goat. It is dissolved by alcohol in all proportions, and is soluble in 6 parts of water at 68° .

When butter is melted with water, buttermilk, cheese and

other impurities are separated from it, and the pure oil rises to the surface. It consists of margarine, oleine, butyrine, caprone, and caprine. The three latter are in small quantity, but it is to them, that the peculiar pleasant smell and taste of fresh butter are owing. They are compounds of oxide of glyceryl (page 877) with butyric, caproic and capric acids.

Hircic acid, was discovered by Chevreul in the fat of the goat; its composition is unknown.

Phocenic or *delphinic acid*, $\text{HO} + \text{C}_{10}\text{H}_7\text{O}_3$ (Chevreul); another volatile acid contained in train oil or seal oil, and in the berries of *Viburnum opulus*. Phocenic acid is a colourless liquid which burns like a volatile oil; its taste is nauseous and ethereal, its density 0.932 at $82^\circ.4$, its boiling point above 212° ; it dissolves in 18 parts of water at 86° .

All these volatile acids are obtained in the same way. The fat oil which they accompany is saponified by an alkali, and the soap decomposed by an excess of tartaric acid, in which the volatile acids are soluble, and may thus be separated from the fat insoluble acids. The volatile acid is then converted into a salt of barytes by adding barytes-water to it, and thus precipitated. The barytic acid is again decomposed by phosphoric or sulphuric acid, and the volatile acid thus set at liberty is rectified by the heat of a water-bath; it is then purified completely from water by means of fused chloride of calcium. These volatile acids form but a small proportion of the butter and oil in which they are found.

Cevadic acid exists in the fat extracted by ether from the seeds of *Veratrum sabadilla*. It forms by distillation a sublimate of white needles of a silky lustre, fusible at 68° (Pelletier and Caventou.) It is named also *sabadillic acid*.

Veratric acid (dried at 212°) $\text{HO} + \text{C}_{18}\text{H}_9\text{O}_7$, is obtained by exhausting the seeds of cevadilla by alcohol and sulphuric acid, and neutralising the alcoholic extract by hydrate of lime; veratrine and other products precipitate, but veratric acid remains in solution combined with lime, and is obtained by decomposing its salt of lime with hydrochloric acid. Veratric acid forms short thin quadrangular prisms, colourless and having a slightly acid taste. Its solubility in cold water is small, but it is more soluble in hot water, dissolves easily in hot alcohol and crystallizes on cooling; it is insoluble in ether. The crystals lose

water at 212° , and become then of a dull white. They fuse at a high temperature into a colourless liquid, and sublime without residue. Fuming nitric acid and concentrated sulphuric acid have no destructive action on veratric acid (Merck). The alkaline *veratrates* are crystallizable, and very soluble in water and alcohol; the salts of lead and silver are insoluble in water, but soluble in alcohol. *Veratric ether*, $\text{EO} + \text{C}_{18}\text{H}_9\text{O}_7$ (Dr. Will), is a crystalline radiated, very friable mass, of density 1.14.1, fusing at $107^{\circ}.6$ (42° centig.), and imperfectly volatile.

Crotonic acid, termed also *Iatrophic acid*, is derived from croton oil, the fat oil of the seeds of *Croton tiglium*, in the same way as the preceding acid. It is solid, very volatile and highly poisonous (Pelletier and Caventou).

SECTION V.

OILY ACIDS OF BUTTER OF COCOA, BUTTER OF NUTMEGS, AND PALM OIL.

Cocinic acid, termed also *Cocostearic acid*, $\text{HO} + \text{C}_{27}\text{H}_{26}\text{O}_3$ (Bromeis) is the crystallizable acid of the butter of the cocoa-nut. This butter is obtained by expressing the dry fruit between hot plates; it is white and possesses the consistence of fat, and is distinguished from other fatty bodies by its great solubility in alcohol.

The mode of preparing cocinic and all the other oily acids is similar. The butter of cocoa is boiled with a solution of an alkali, and thus saponified; the soap is then decomposed by a mineral acid, and the concrete fat acids which appear are expressed repeatedly between folds of blotting paper, till the latter no longer absorbs liquid matter. The expressed solid matter is saponified anew with soda, the soap dissolved in water, and separated by dissolving common salt in the water; the soap thus prepared is again decomposed by tartaric acid. Finally the fat acid thus obtained is purified by crystallizing it repeatedly from alcohol till its point of fusion becomes fixed (Liebig). Cocinic acid is inodorous, of a brilliant white, fuses at 95° , and forms on cooling an amorphous diaphanous mass, like porcelain, is insoluble in water. It may be distilled without change. The *cocinates* of alkaline bases considerably resemble the soaps of the other oily acids.

Sericic or *Myristic acid*, $\text{HO} + \text{C}_{28}\text{H}_{26}\text{O}_3$ (Playfair). This acid is obtained from the solid portion of the butter of nutmegs, the fruit of *Myristica moschata*, in which it is combined with glycerine. This solid portion dissolves completely in 4 parts of boiling alcohol, by which it may be easily distinguished from other soluble fat bodies, and gives, on the cooling of the liquid, the sericate of glyceryl in thin silky needles.

Sericic acid, which was discovered by Dr. Playfair, crystallizes in white brilliant plates, of a silky lustre, (hence the name, sericic acid); it fuses between $118^{\circ}.4$, and $120^{\circ}.2$ (48° and 49° centig.), and on cooling becomes a mass, having a very distinct crystalline structure. It is very soluble in alcohol and ether, insoluble in water. It is decomposed by dry distillation, and violently attacked by nitric acid. *Sericates* of alkaline bases are distinguished from other soaps by crystallizing from alcohol; their solutions do not become viscid and thready by concentration, nor are they disturbed by the addition of much water (Playfair). Sericic ether is an oily, colourless liquid, of density 0.864. *Sericine*, or sericate of glyceryl, contains as base oxide of glyceryl minus 2HO , or $\text{C}_6\text{H}_5\text{O}_3$; its formula being $\text{C}_{118}\text{H}_{113}\text{O}_{15} = 4 (\text{C}_{25}\text{H}_{27}\text{O}_3)$.

Palmitic acid, $\text{HO} + \text{C}_{22}\text{H}_{31}\text{O}_3$ (Fremy, Stenhouse). A soap of the palm oil of commerce yields when decomposed by an acid, a mixture of palmitic and oleic acids; which mixture, dissolved in boiling alcohol, gives crystals of palmitic acid on cooling. Purified by repeated crystallization from alcohol, palmitic acid forms brilliant plates, which completely resemble those of margaric acid, and have the same point of fusion, 140° ; it is insoluble in water. It dissolves in alkaline carbonates, and forms a transparent emulsion. After being heated to 572° (300° centig.), palmitic acid does not crystallize from alcohol in leaflets, but in mammillated masses, which, however, have precisely the same composition (Fremy). Palmitic acid distils with very little alteration. Chlorine decomposes the acid when heated, and yields several chlorinated products, which are less fluid, and acid, but do not combine with bases without losing their chlorine. Palmitate of glyceryl or *palmitine*, when pure is crystalline, and of brilliant whiteness, is very slightly soluble in boiling alcohol, but dissolves in boiling ether in all proportions, and is deposited, on cooling, in extremely small crystals. From the analysis of Dr. Stenhouse, palmitine is represented by

$C_{35}H_{33}O_4$, which is anhydrous palmitic acid $C_{32}H_{31}O_3$ plus C_3H_2O ; the last formula expressing half an equivalent of anhydrous oxide of glyceryl, $C_6H_7O_5$, from which $3HO$ have been subtracted.*

Ethalic acid (page 880), termed also cetylic acid, has absolutely the same composition as palmitic acid.

MARGARIC AND STEARIC ACIDS.

Margaric acid, or *Margarylic acid*, $2HO + C_{68}H_{66}O_6 = 2HO + 2(C_{34}H_{33} + O_3)$; in the last formula $C_{34}H_{33}$ represents a radical margaryl (Liebig). This acid forms the principal part of the stearopten, or solid portion of human fat and vegetable fixed oils; it is also produced by the dry distillation of ox and mutton suet, and of stearic acid. It is most easily obtained in a state of purity, by boiling for some minutes stearic acid (the matter composing stearine candles), with an equal weight of nitric acid, of density 1.273 (32° Baumé). The mixture is then left to itself, and after expressing the product, which has become concrete on cooling, between folds of blotting paper, it is crystallized several times successively from alcohol, till its point of fusion remains constant at 140° (60° centig.). It may also be obtained by adding acetate of lead to the solution of a soap of olive oil, or of human fat; on treating the precipitate which falls, by cold or hot ether, margarate of lead remains in a state of purity, being insoluble in that menstruum. This salt gives margaric acid, when heated with a dilute mineral acid. (Liebig's *Traité*). Margaric acid was so named by Chevreul from its pearly lustre; in external aspect it greatly resembles stearic acid, but is more fusible, the last acid fusing between 158° and 167° (70° and 75° centig.).

Margarates.—In the formation of salts of margaric acid, sometimes both its atoms of water, and sometimes only one is replaced by another base. The *ether* of margaric acid, which contains 2 atoms of oxide of ethyl (Varrentrapp), is obtained by saturating with hydrochloric acid gas an alcoholic solution of margaric acid, and withdrawing the excess of hydrochloric acid by washing the product with water. It fuses at 71°.6, is decomposed by alkalies and their carbonates, and also by dry distillation. A mixed soap of oleate and margarate of

* Phil. Mag. 3rd series, xviii. 186.

potash or soda, such as that of olive oil, when dissolved in about eight times its weight of hot water, and the solution afterwards diluted by fifty times its bulk of water, allows an *acid margarate* of potash or soda to precipitate, which may be purified from a little oleate with which it is contaminated by repeated crystallization from alcohol. This salt contains 1 atom of water, and 1 atom of potash as base. Both the acid and neutral margarates of potash crystallize from an alcoholic solution in plates, which have less lustre than the corresponding stearates. *Margarine*, or the margarate of glyceryl, has not been analysed in a state of purity. The solid matter which is formed in olive oil when cold, is a combination of margarate and oleate of glyceryl, according to Pelouze and Boudet.

Stearic acid, hypomargarylic acid, $2\text{HO} + \text{C}_{68}\text{H}_{66}\text{O}_5 = 2\text{HO} + 2(\text{C}_{34}\text{H}_{33}) + \text{O}_5$.—This acid was discovered by Chevreul, combined with oxide of glyceryl in animal and vegetable fats and in the bile of many animals. It may be obtained pure by crystallizing the stearic acid of commerce from alcohol, till its point of fusion is between 158° and 167° . The latter substance, which forms the stearine candles of commerce, is obtained by saponifying tallow with hydrate of lime, to get rid of its oxide of glyceryl which being set free dissolves in water, and decomposing the insoluble soap of lime with dilute and boiling sulphuric acid. The oleic acid is separated from the stearic acid by submitting the latter to pressure between hot metallic plates. The cake thus obtained is said to contain not more than traces of margaric and oleic acids. Mixed stearic and oleic acids may also be separated by solution in boiling alcohol, from which the stearic acid crystallizes out, and may be purified by successive crystallizations from alcohol.

Stearic acid crystallizes by cooling in white brilliant needles, soft to the touch, pulverisable and insoluble in water. When fused and cast in a mould its surface is rough from crystalline granulation, but if a minute quantity of finely pulverised talc (French white) be mixed with the melted acid, it then solidifies with a perfectly smooth and glossy surface like that of wax. Arsenious acid was improperly used at one time to produce the effect described in stearine candles. Stearic acid fuses at 167° , and solidifies at 158° (Chevreul); its density when solid is 1.01, in the liquid condition 0.854. It is tasteless

and inodorous, fused by heat or dissolved in alcohol it reddens litmus; it dissolves in its own weight of ether of density 0.727, when heated in air it burns like wax. Stearic acid is decomposed by dry distillation, and resolved into margaric acid and oxide of margaryl. Nitric acid with heat decomposes it producing first margaric acid, and afterwards suberic and succinic acids. Stearic acid is dissolved entirely by sulphuric acid with a gentle heat, without coloration, and is precipitated on the addition of water in the form of white flocks. It may thus be separated from sulphate of glyceryl, and in a great measure from oleic acid.

Stearates.—Stearic acid is bibasic and forms two classes of salts in which one or both of its basic atoms of water are replaced by a metallic oxide. In the cold, stearic acid only decomposes the alkaline carbonates partially, so as to produce a bistearate and bicarbonate, but with heat it decomposes the same carbonates completely. The neutral stearates of alkaline bases dissolve without alteration in 10 or 20 parts of hot water, but the addition of a large quantity of water causes decomposition, and an acid stearate precipitates while the liquid becomes strongly alkaline; the cooling of a hot solution of a stearate in a small quantity of water is attended with the same decomposition, and causes the whole mass to assume a gelatinous consistence. The *acid* stearate of potash contains $\text{HO} + \text{KO}$ as base; obtained by precipitation of the neutral stearate in solution by 1000 parts of cold water, and crystallized from alcohol it forms white pearly plates. Boiling water still farther decomposes this stearate, 1000 parts of the former producing with the latter a turbid and viscid liquid, which becomes liquid and transparent at 167° , and deposits pearly plates between $138^{\circ}.2$ and $78^{\circ}.8$ (59° to 26° centig.); 3 atoms of the acid salt are then resolved into 1 atom of the neutral stearate of potash (containing 2KO as base) which remains in solution, and into a *bistearate* of potash (containing $\text{KO} + 3\text{HO}$ as base to 2 atoms of acid), which remains in suspension in the liquid. Again, by the cooling of the solution of the neutral stearate of potash, a portion of the former acid stearate of potash is deposited, and half of the alkaline base remains in solution. The precipitate is therefore a mixture of bistearate and acid stearate of potash. If exposed again to boiling water it ends by being converted

entirely into bistearate. The solutions of the stearates of alkaline bases are precipitated by salts of all the other metallic oxides, insoluble stearates being formed.

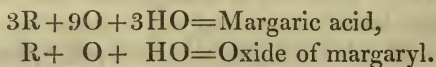
Stearine, or the acid stearate of oxide of glyceryl is the essential part of all kinds of suet; it may be obtained by fusing purified mutton suet by a water bath, dissolving it in 8 or 10 times its volume of ether, allowing the solution to cool, which becomes a thick mass, and washing the expressed solid matter with ether. It forms white pearly plates, fuses at 140° or $143^{\circ}.6$ (60° or 62° centig.), and on cooling again forms a solid pulverisable mass which is not crystalline. It dissolves in 6 or 7 parts of boiling alcohol. This stearate in combination with the oleate of glyceryl forms the solid portion of the butter of cacao. According to the analysis of Liebig and Pelouze, stearine may be represented by $C_6H_7O_5.HO.C_{68}H_{66}O_5 + H_2O$, or by 1 atom of hypomargarylic acid combined with 1 atom of oxide of glyceryl and 1 atom of water as bases, with an additional atom of water of crystallization.

PRODUCTS OF THE DRY DISTILLATION OF MARGARIC AND STEARIC ACIDS.

Stearic acid distilled in a vessel about two thirds filled with the acid, yields first a white solid product, which fixes at $156^{\circ}.2$ (69° centig.), and is a mixture of margaric acid fusible at 140° , of a crystalline neutral body margarone fusible at $170^{\circ}.6$, and of a liquid hydrocarbon in small quantity. The last half of the distilled product is generally softer and accompanied with inflammable gases; and towards the end the residue blackens and assumes the consistence of tar. When stearic acid is distilled with one fourth of its weight of quicklime, a soft buttery mass is obtained, consisting in a great measure of the liquid hydrocarbon and margarone. The products of the distillation of margaric acid are similar. (Redtenbacher and Varrentrapp.)

Margarone, $C_{33}H_{33}O$, was discovered by Bussy. It is formed by the dry distillation of margaric and stearic acids alone or mixed with quicklime; it may be freed from adhering margaric acid by caustic ley in which margarone is insoluble, and purified by crystallization from alcohol. It is a white very friable pearly mass, and becomes electrical by friction. It is volatilised

completely from a slip of platinum, but when distilled in a retort it leaves a residue of charcoal. It is soluble in 50 parts of alcohol of 0.837, and in $6\frac{1}{2}$ parts of absolute alcohol, and crystallizes upon the cooling of these solutions. Margarone is also soluble in ether, concentrated acetic acid, oil of turpentine and the liquid fats. Obtained from the distillation of stearic acid and lime, the point of fusion of margarone may rise so high as $186^{\circ}.8$ (86° centig.) after repeated crystallization, it must be then a different substance. From the analyses of margarone fusing at $170^{\circ}.6$ by Bussy, Redtenbacher and Varrentrapp, which agree, it follows that margarone is produced when margaric acid loses the elements of 1 atom of carbonic acid. Margarone is also produced in the distillation of stearic acid, and it is supposed possible by M. Liebig that the carbonic acid may come from the decomposition of the margarone. 2 atoms of hydrated stearic acid, which, indicating $C_{34}H_{33}$ by R, would be $R_4O_{10} + 4HO$, are resolved into—



Two atoms of oxide of margaryl (a hypothetical compound) would contain the elements of a hydrocarbon $C_{66}H_{66}$, of 1 atom carbonic acid CO_2 and 1 atom of carbon C.

The matter fusible at $186^{\circ}.8$, which Bussy named *stearone* may from his analysis be represented by $2R + O$.

ACID PRODUCTS OF THE ACTION OF NITRIC ACID ON MARGARIC AND STEARIC ACIDS.

When stearic acid is heated with an equal volume of nitric acid of 1.284, an abundant disengagement of deutoxide and peroxide of nitrogen takes place as soon as the mixture boils. If the mixture is then allowed to cool the stearic acid separates apparently unaltered, but really converted entirely into margaric acid, while the nitric acid contains no foreign substance in determinable quantity. By the prolonged action of the boiling acid on margaric acid, the latter is gradually but completely dissolved, and the more readily if the nitric acid be renewed from time to time; the solution then contains suberic acid,

succinic acid and an oily substance soluble in nitric acid. (Bromeis.)

Suberic acid, $\text{HO} + \text{C}_8\text{H}_6\text{O}_3$.—Brugnatelli first obtained this acid by the action of nitric acid upon cork (page 759). It is prepared by evaporating the solution of stearic or margaric acid in nitric acid to one half and allowing it to rest; the solution in 24 hours becomes a semi-solid mass, which is thrown into a funnel to drain, and washed with cold water. When expressed and crystallized several times it forms pure suberic acid. Suberic acid when humid fuses between 122° and $129^\circ.2$ (50 to 54° centig.), but when dried in air or in vacuo, between $244^\circ.4$ and 248° (118 to 120° centig.); it is distilled without alteration. Suberic acid is sparingly soluble in cold water, but dissolves in 1.87 parts of boiling water, in 0.87 of boiling alcohol, also in 10 parts of cold and 6 parts of boiling ether. Suberate of lime distilled with an excess of quick-lime gives among other products a colourless liquid, which boils at 374° , and remains liquid at 10.4° (-12° centig.), of which the composition is expressed by $\text{C}_8\text{H}_7\text{O}$.

Succinic acid, $\text{HO} + \text{C}_4\text{H}_2\text{O}_5$; and when sublimed $\text{HO} + 2\text{C}_4\text{H}_2\text{O}_3$. This acid has long been derived from the distillation of amber (page 904) and exists according to several observers in the resin of some *Coniferae*. The mother liquor which remains after the separation of suberic acid in the process described above, contains succinic acid soiled with suberic acid. The solution with the washings of the suberic acid is evaporated to crystallization, the product dried and treated with ether in the cold, which easily dissolves suberic acid while it leaves the succinic acid behind in a great measure. The latter may be purified completely by sublimation.

The crystals of succinic acid are colourless and inodorous, of density 1.50, have a somewhat acrid taste, and sublime without decomposition. This acid may be obtained quite anhydrous by several distillations, and then condenses as drops in the receiver. The hydrated acid dissolves in 2 parts of boiling and 5 parts of cold water; it is equally soluble in alcohol and ether. Hydrated succinic acid sublimes at 284° ; fuses at 356° losing one half of its water, and boils at 455° . This acid is not sensibly affected by chlorine or nitric acid; added to potash in fusion it gives oxalic acid. Hydrated succinic acid absorbs the

vapour of anhydrous sulphuric acid, and the compound losing the elements of one atom of water forms a new acid, of which the salt of lead is expressed by $4 \text{ PbO} + \text{C}_8\text{H}_2\text{S}_2\text{O}_{10}$.

Succinates.—The constitution of this class of salts is still doubtful. According to Fehling the acid is really tribasic, $3\text{HO} + \text{C}_8\text{H}_3\text{O}_5$; the basic salt of lead dried at 428° being $3\text{PbO} + \text{C}_8\text{H}_3\text{O}_5$. In the salt of silver and other succinates only two atoms of metallic oxide are found, the third atom of base being water. Neutral succinate of *ammonia* is much used to separate peroxide of iron from oxide of manganese and other metallic oxides; both the reagent and metallic solution must be exempt from free acid, as otherwise the succinate of iron will dissolve in the washings. The formula of *succinamide* is $\text{NH}_2 + \text{C}_4\text{H}_2\text{O}_2$, of *bisuccinamide* $\text{NH}_2 + \text{C}_8\text{H}_3\text{O}_4$. The last compound when dissolved in water assumes 2HO , and forms fine rhomboidal crystals; the solution of these crystals has no action upon metallic salts, and therefore does not contain succinic acid.

SECTION II.

OLEIC ACID AND ACIDS RELATED TO IT.

This acid has been less successfully investigated than stearic acid, and is probably a mixture of two different principles as it is generally obtained. It forms the essential part of the fat oils which are not drying, such as oil of olives and oil of almonds, from the last of which it is most advantageously prepared, and is found in less considerable quantity in tallow, solid fats, human bile and old cheese. The acid derived from a soap of the fat oil of sweet almonds is mixed with its weight of pulverised oxide of lead, and after the mixture is digested on a water-bath for several hours, twice its bulk of ether is added to it, and the whole left to itself for 24 hours. There is thus formed margarate of lead which is insoluble, with an acid oleate of the same base, which is soluble in ether. The ethereal solution is then decomposed by dilute hydrochloric acid, which sets at liberty the oleic acid; the last coming to the surface of the mixture with the ether, and forming an oily limpid stratum. The ether is expelled by evaporation, and the oleic acid saponi-

fied by an alkali. The soap is purified by dissolving it in water and separating it by means of common salt; these operations being several times repeated. At last, when the soap is colourless, it is dissolved in water and decomposed by tartaric acid; the oleic acid thus liberated is washed with boiling water, and dried by the water-bath (Liebig's *Traité*, ii.). It may be prepared by the same process from the liquid product obtained in the manufacture of stearine candles. The formula for oleic acid established by M. Varrentrapp is $C_{44}H_{39}O_4$.

Oleic acid forms an oil which is colourless or of a yellowish tint, has a very weak odour, an acrid taste, reddens litmus strongly, is lighter than water, and becomes a mass composed of crystalline needles a few degrees above the freezing point of water. It is insoluble in water, but mixes with alcohol of 0.822 in all proportions. Sulphuric acid colours oleic acid. Nitric acid with oleic gives suberic acid, among other products, but no oxalic acid. Peroxide of nitrogen or nitrate of suboxide of mercury transforms oleic acid into elaidic acid.

Oleates.—Oleic acid decomposes the alkaline carbonates; its compounds are soft, have the appearance of soap and dissolve better in alcohol than in water. *Oleine*, the oleate of oxide of glyceryl, forms the greater portion of the fat oils and of most of the solid fats found in nature. It is mixed in these with margarine or stearine, either of which is deposited in the solid state, when the oil is exposed to great cold, the oleine may then be separated by expression of the solid matter, although never in a state of purity. According to Pelouze and Boudet there are two species of oleine, the liquid portion of such fats as are not drying but disposed to become rancid, differing from the liquid portion of the drying oils, in solubility, and particularly in the transformation which it undergoes under the influence of hyponitric acid into elaidine and elaidic acid, while the oleine of drying oils undergoes no sensible alteration in the same circumstances. The neutral oleate of *potash* is deliquescent in a damp atmosphere, dissolves completely in 4 parts of water, forming a viscid syrup, and is decomposed by a greater excess of water and resolved into potash and an acid oleate of potash. The latter salt is insoluble in water, but dissolves easily in hot or cold alcohol. Oleate of *soda* dissolves in 10 parts of water at 89°.6. Oleate of *lead* is soluble in ether.

Sebacic acid, $\text{HO} + \text{C}_{10}\text{H}_8\text{O}_3$. Oleic acid from both the drying and non-drying oils, from tallow and every other source, affords among the products of its dry distillation a matter which becomes concrete on cooling and is sebacic acid, easily recognised by its solubility in water and its property of giving a white precipitate with a salt of lead. This acid is prepared by washing with boiling water the solid and liquid products of the distillation of oleic acid or any of the fats which contain oleic acid, so long as the solution gives crystals on cooling. These crystals are washed with cold water, and crystallized repeatedly from boiling water till they are colourless and free from empyreumatic odour.

Sebacic acid greatly resembles benzoic acid in appearance, and crystallizes in white very light plates or needles of a pearly lustre; it reddens litmus and has an acid taste, loses nothing at 212° , fuses at 260.6° , and sublimes at a higher temperature without alteration. It is but sparingly soluble in cold water, but dissolves easily in boiling water and also in alcohol and ether.

Sebates.—The solution of sebacic acid throws down white precipitates from salts of silver and lead. The sebates of the alkaline bases are very soluble. *Sebacic ether* has been formed in the usual way, by transmitting a stream of hydrochloric acid gas through an alcoholic solution of sebacic acid.

Elaïdic acid, $\text{C}_{72}\text{H}_{66}\text{O}_5$. When a non-drying oil is mixed with nitrate of suboxide of mercury or with peroxide of nitrogen, it gradually becomes solid. This change is due to the transformation of the oleic acid of the oil into elaïdic acid, which remains in combination with oxide of glyceryl, forming *elaïdine* or the elaïdate of glyceryl, which is solid and crystalline at the usual temperature. When nitrate of mercury is used in this experiment a portion of the mercury is reduced. To prepare elaïdic acid, peroxide of nitrogen produced by the action of nitric acid on starch is carried through oleic acid free from margaric acid, in a vessel surrounded by cold water. The oleic acid after a time concretes into a mass composed of considerable leaflets, which is washed with boiling water, then dissolved in an equal bulk of alcohol and left to crystallize. Pearly crystals in tables are obtained, which are expressed between folds of blotting paper and crystallized several times from alcohol (Meyer). Elaïdic acid forms thin leaflets of a silvery lustre,

considerably resembling benzoic acid. This acid is insoluble in water, sparingly soluble in ether, but highly soluble in alcohol, particularly when hot; the alcoholic solution reddens litmus strongly. Elaïdic acid appears to distil without change. It decomposes alkaline carbonates and forms salts which dissolve in 6 or 8 parts of water, producing a transparent very thick emulsion. These salts may be crystallized from alcohol.

Oleic acid, when treated with nitric acid, gives rise to a series of acid products, discovered by Laurent, many of whose results have since been confirmed by Bromeis. These are, in addition to suberic acid, *azelaic acid*, $\text{HO} + \text{C}_{10}\text{H}_8\text{O}_4$, an acid isomeric with suberic acid, and closely resembling it; *pimelic acid*, $\text{HO} + \text{C}_7\text{H}_5\text{O}_3$, which crystallizes in white hard grains; *adipic acid*, $\text{HO} + \text{C}_6\text{H}_4\text{O}_3$ (Laurent), or $2\text{HO} + \text{C}_{14}\text{H}_9\text{O}_7$ (Bromeis); *lipic acid*, when crystallized, $\text{HO} + \text{C}_5\text{H}_3\text{O}_4$, when sublimed $\text{C}_5\text{H}_3\text{O}_4$; *azoleic acid*, $\text{C}_{13}\text{H}_{13}\text{O}_4$.

When oleic or elaïdic acid is heated to dryness in a silver capsule with three times its bulk of strong potash ley, the mass being continually stirred till it becomes dry, and heated till the potash begins to fuse, the materials swell considerably, and much hydrogen gas is evolved. The yellowish-brown saline mass contains a new fat acid, besides much acetic acid. This acid, which is the same from both oleic and elaïdic acid, crystallizes when separated in thin needles of brilliant whiteness, fusible at $143^{\circ}.6$ (62° centig.). It has been studied by M. Varentrapp, who represents it by $\text{HO} + \text{C}_{32}\text{H}_{30}\text{O}_3$; which differs only from palmitic and ethalic acids by containing an atom less of hydrogen.

ACIDS OF CASTOR OIL.

Castor oil differs considerably from the other fixed oils, particularly by its solubility in alcohol. A soap of this oil, when decomposed by a mineral acid gives a solid and a liquid oily acid. The first is termed *margaritic acid* by Bussy and Lecanu; it fuses at 266° ; the second is named *ricinic acid*.

Nitric acid gives with castor oil an acid, named *œnanthylic acid* by Mr. Tilley, from its relation in œnanthic acid." The formula of œnanthylic acid is $\text{HO} + \text{C}_{14}\text{H}_{13}\text{O}_3$ (Tilley). Ac-

according to Bromeis, cœnanthylic acid is identical with the azoleic acid of Laurent.

Castor oil solidifies with nitrate of suboxide of mercury, or with peroxide of nitrogen, and forms a yellow transparent mass like wax. The mass washed with water and dissolved in boiling alcohol furnishes *palmine* in confused crystalline grains. Alkalies saponify palmine like elaïdine, disengaging glycerin, and combining with *palmic acid*. This acid, when pure, crystallizes in white silky needles, grouped about a common centre, is fusible at 122°, and dissolves with facility in alcohol and ether. Palmine and palmic acid are also formed by the action of sulphurous acid gas on castor oil.

ACIDS FORMED BY THE ACTION OF SULPHURIC ACID ON THE FAT OILS.

When sulphuric acid is added in small proportion to fat oils, its action is limited to the abstraction of their glycerin, with which it combines and forms sulphoglyceric acid (page 878), while the oily acids are set at liberty. Such is the reaction that occurs when tallow or hog's lard is mixed with half its weight of sulphuric acid. But when the proportion of sulphuric acid is increased, particular compounds of that acid with the oily acids are produced, which dissolve in water. The compounds thus formed by acting upon olive oil with concentrated sulphuric acid have been carefully studied by M. Fremy.*

Oleic acid and concentrated sulphuric acid combine directly, and form *sulpholeic acid*, a double acid. Pure margaric acid dissolves in sulphuric acid, but does not form a stable compound, for it is separated by water without having undergone any alteration; but when mixed with a certain quantity of oleic acid, both oily acids combine with sulphuric acid, and *sulphomargaric acid* is formed with sulpholeic acid. These two compounds are equally formed, together with sulphate of glycerin, when half a volume of concentrated sulphuric acid is cautiously added by small quantities, to olive oil, any elevation of temperature being guarded against. If then mixed with twice its

* Ann. de Chim. et de Phys. t. lxxv, p. 113.

volume of cold water, and left at rest for twenty-four hours, the sulpholeic and sulphomargaric acids being insoluble in dilute sulphuric come in the form of a syrup to the surface of the liquor, while the sulphate of glycerin remains in the strongly acid liquid below. After the mixture of sulpholeic and sulphomargaric acids is washed with a little water, it is dissolved entirely in a large quantity of water. The solution has an acid and fatty taste, with a bitter after-taste, may be neutralised by an alkali without decomposition, and the salt thus formed occasions in metallic solutions precipitates insoluble in water, and slightly soluble in alcohol.

Left to itself, the mixture of sulpholeic and sulphomargaric acid undergoes decomposition; when the solution is made to boil, the decomposition is instantaneous. The sulphuric acid then separates from the elements of the oleic and margaric acids, and these last are themselves transformed into new acids; the margaric acid yielding *metamargaric acid* and *hydromargaritic acid*, the oleic acid, *metoleic acid* and *hydroleic acid*. A compound of hydromargaritic and metamargaric acid, which has the properties of a single acid, has been named *hydromargaric acid*, by Fremy. These compounds are oily bodies insoluble in water, of which those related to margaric acid are solid, and those related to oleic acid liquid at ordinary temperatures. These acids have been also examined by Varrentrapp and by Mr. Miller, but their composition is still involved in considerable uncertainty.

When metoleic and hydroleic acids are distilled, they are decomposed and resolved into two hydrocarbons of the olefant gas type; *elaène*, $C_{18}H_{18}$, a white substance, boiling at 230° , and *oleène*, $C_{12}H_{12}$, a colourless ethereal liquid. Elaène combines with chlorine, with the evolution of hydrochloric acid, and forms an oily compound (Fremy).

ACROLEINE.

Oils and fats boil at a high temperature, giving off carbonic acid with a little inflammable gas, and a substance possessed of a most pungent odour, which attacks the eyes most painfully, and is named acroleine. The pure oily acids do not yield this substance, but only their compounds with oxide of glyceryl,

proving that the acroleine comes from the glycerin. It is, indeed, produced in large quantity by the distillation of pure glycerin. Hence the occurrence of acroleine among the products of the distillation of a fat or oil is a sure and delicate test of the presence of glycerin in the oil.

Acroleine is unknown in a state of purity. It absorbs oxygen with great rapidity from the air and becomes acid. Its solution is decomposed even in close vessels, and yields a tasteless, inodorous, and very indifferent white solid, not resembling fat, and insoluble in all menstrua yet tried. No compound of acroleine has been formed from which it can again be obtained. (Liebig).

CHAPTER IX.

VEGETO-ALKALIES.

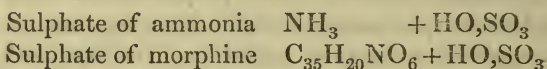
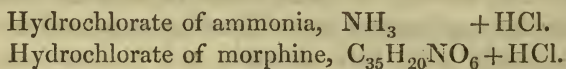
IN the class of organic bases are included a number of bodies containing nitrogen, which have the properties of the basic or metallic oxides, and form salts with acids. These salts perfectly resemble salts of metallic oxides; the acids which they contain continue to be affected by the usual reagents, sulphate of morphine and sulphate of soda being equally precipitated by chloride of barium, and the organic bases themselves are liberated by stronger bases. Oxide of ethyl and oxide of methyl are likewise bases, but in salts of these, acids have their properties disguised, and can no longer be transferred to other bases such as the metallic oxides, by double decomposition; the compounds of the last mentioned bases with acids diverge therefore widely in their properties from common salts. The present class of organic basis are principally derived from plants, and are known as the *vegeto-alkalies*. The solutions in water of such of them as are soluble in that liquid, and their solutions in alcohol restore the blue colour of reddened litmus and render yellow turmeric paper brown; they are therefore unequivocally alkaline. The following organic bases appear to be allied to the class of *vegeto-alkalies*, *ammeline*, *melamine*, *aniline* or *crystalline*, *urea*, with certain bases still problematical which Unverdorben

derived from volatile animal oil (oil of Dippel), namely odorine, ammoline and animine.

The investigation of this class of bodies was commenced by Derosne, who in 1803 observed narcotine, and by Sertuerner, who, in 1817, recognised in morphine from opium the first vegetable base. These chemists were followed by others, particularly Robiquet and MM. Pelletier and Caventou, who in cinchona bark, nux vomica, and other vegetable matters found organic bases, in which the medicinal virtues of the plants resided. The analogy of these bases to metallic oxides and their valuable applications in medicine have rendered the class a favourite study with both chemists and pharmacians. The method generally pursued in the preparation of such of these bases as, like morphine, are insoluble in water, consists in treating the vegetable substance containing the base with a dilute acid which forms a soluble salt with the base. This solution is concentrated by evaporation, and slightly supersaturated with a soluble alkali, ammonia, hydrate of lime, magnesia or carbonate of soda, by which the vegetable base is precipitated coloured and in an impure condition. To free it from foreign matters, the base or a salt of it is crystallized from alcohol, or if neither the base nor its salt is not much more soluble in hot than in cold alcohol, and therefore does not crystallize well from that liquid, the salt is rendered white by treatment with animal charcoal and repeated crystallization, and the pure base finally precipitated by means of carbonate of soda.

The extraction of bases which are soluble in water and volatile such as conicine, is more difficult. The leaves, flowers, root, or seeds which contain the volatile base are submitted to distillation with a weak solution of caustic alkali. The water which distils over is found to be saturated with the organic base, and generally contains besides a quantity of ammonia resulting from the decomposition of a portion of the former. The distilled water is fully neutralised with dilute sulphuric acid, mixed in a concentrated state with caustic alkali, and the whole digested in a close vessel with ether, which last solvent takes up the liberated vegetable base and the ammonia. The ethereal solution being then distilled by the heat of a waterbath, the ether and ammonia escape, and the vegetable base is left pure in the retort.

Ammonia is a true type of the organic bases in general containing nitrogen. Morphine, quinine, and other members of the class unite directly with hydrochloric acid, as ammonia does, without the separation of water. An atom of water likewise enters into the composition of all their salts containing an oxygen acid, as in the corresponding salts of ammonia. This will appear on comparing together the following formulæ, in which morphine $C_{35}H_{20}NO_6$ appears exactly equivalent to ammonia NH_3 :



Urea even does not form an exception to this rule, but combines directly with hydrochloric acid, according to the observation of Hagen. The hydrochlorates of the vegetable bases also resemble sal ammoniac in forming a crystallizable double salt with one atom of bichloride of platinum, and with two atoms of chloride of mercury, the last corresponding with sal alem-broth. This similarity in properties favours the idea that these bases may have a constitution analogous to that of ammonia or be amides of an unknown radical, as ammonia is the amide of hydrogen. The amides derived from most acids are neutral substances, it is true, such as oxamide, $NH_2 + C_2O_2$, succinamide $NH_2 + C_4H_2O_2$, fumaramide, $NH_2 + C_4HO_2$ and benzamide $NH_2 + C_{14}H_5O_2$. Urea, however, which contains two atoms of amidogen, as it is represented by Dumas, $2NH_2 + C_2O_2$ has a basic character ; and melamine is strongly basic, which may be represented as $Cy_3 + 3NH_2$, as cyanuric acid is $Cy_3 + O_3$ (Liebig). But although this view of the constitution of vegeto-alkalies is not improbable it must be admitted that the radicals which are thus supposed to be in combination with amidogen, in the vegetable bases, have not been transferred from that to any other radical, much less isolated.

Chlorine transmitted through water containing a vegetable base in suspension quickly produces hydrochloric acid, and forms a hydrochlorate of the base, which is soluble in the water.

This salt is decomposed by the continued application of chlorine, generally with a change of colour in the liquid to yellow or red, and the formation of a precipitate. The precipitate from the salts of strychnine has been found to contain both chlorine and nitrogen. Quinine and cinchonine salts become with chlorine yellow, rose-red, and then violet-red, while a red resinous matter precipitates, which in the air becomes brown, hard, and pulverisable. But the nature of the changes which chlorine produces upon these bases remains still to be investigated. The action of iodine is more definite. According to Pelletier, 2 parts of strychnine and 1 part of iodine dissolved in boiling alcohol, give a precipitate on cooling, of yellow crystalline spangles, resembling mosaic gold, and hydriodate of strychnine crystallizes out from the liquor when concentrated by evaporation. The precipitate appears to contain $1\frac{1}{2}$ equivalent of iodine. The precipitate produced in brucine, treated with tincture of iodine in the same way is yellow; quinine and cinchonine give saffron plates by evaporation of the liquid. The vegetable alkalies are recovered unaltered from these precipitates, when they are treated with a dilute acid, iodine being then liberated or by the action of a solution of caustic potash or soda, and then iodide of potassium or sodium is produced at the same time. The substance thrown down by the action of iodine upon morphine is of a brown colour and differs in nature from the other products as morphine can in no way be revived from it. The hydrogen of the hydriodic acid formed with the other alkalies appears to come from the water, but to be derived in the last case from the decomposition of the vegetable base itself.

Little is known of the action of acids upon the vegetable bases, with the exception of some observations of change of colour which have been made. Thus brucine with a slight excess of nitric acid becomes blood-red, while the colour of pure strychnine is not changed by the same treatment, so that the presence of brucine in strychnine can in this way be detected. Nitric and iodic acids colour morphine, and its salts rose-red. Other bases, such as urea and melamine are decomposed by the stronger acids; urea being converted by the action of concentrated sulphuric acid into carbonic acid and ammonia, by the assumption of two atoms of water; and melamine into cyanuric acid and ammonia, by the assumption of three atoms of water. Thebaine also, exposed to dry hydrochloric

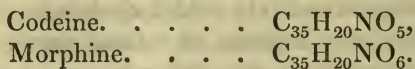
acid gas, is resolved into sal ammoniac and a resinous substance having acid properties (Kane) ; but the other vegetable bases are not found to undergo similar decompositions when exposed to acids.

Curious relations in composition exist between some of the vegetable bases ; thus cinchonine and quinine appear only to differ from each other, in the latter containing an atom of oxygen more than the former :

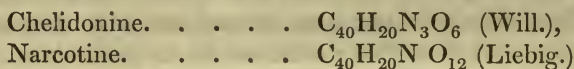


Another base, *aricine*, of which the composition is less certainly determined belongs properly to the same group, containing an atom more of oxygen than quinine, that is, $\text{C}_{20}\text{H}_{12}\text{NO}_3$ (Pelletier). These three bases are found together in the quinquinas.

Codeine and morphine, which are found together in opium, appear to have a similar relation in composition to each other :

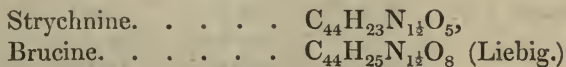


Narcotine from opium and chelidonine, a base likewise from the family of *Papaveraceæ*, appear to be related :

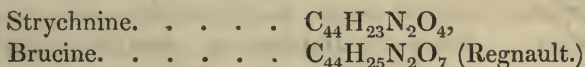


The chelidonine contains 2 atoms of nitrogen more than the narcotine, while the latter contains 6 atoms of oxygen instead of this nitrogen ; these being equivalent quantities, it will be remembered of the elements in question. Or, by adding 2 atoms of ammonia to narcotine and subtracting therefrom 6 atoms of water, chelidonine would be produced (Liebig). Attempts, however, which have been made to convert one of these bases into the other have not been successful. But the composition assigned above to narcotine is by no means certain. The formula for the same base deduced by M. Regnault from his analysis is $\text{C}_{44}\text{H}_{23}\text{NO}_{13}$; and that deducible from the atomic weight of its double salt with bichloride of platinum is $\text{C}_{48}\text{H}_{24}\text{NO}_{15}$ (Liebig.)

According to the formulæ which M. Liebig is inclined to adopt for the two bases strychnine and brucine, which also occur together, the latter contains 2 atoms of water and 1 atom of oxygen more than the former:



To the same bases M. Regnault assigns formulæ which are somewhat different, but which are equally compatible with the atomic weights of these alkalies as observed in their bichloride of platinum compounds:



These formulæ indicate the same difference of composition between strychnine and brucine, as do the preceding formulæ for the same compounds. The composition of thebaine from opium, according to the analysis of Dr. Kane is expressed by $\text{C}_{25}\text{H}_{14}\text{NO}_3$. The composition of jervine, a base discovered by M. Simon in the root of *Veratrum album*, and carefully analysed by Dr. Will is $\text{C}_{60}\text{H}_{45}\text{N}_2\text{O}_5$.

Several other organic bases have been analysed, but those of which the composition has been already stated are perhaps the only ones, for which we have data to construct formulæ of any considerable degree of probability. The numerical results of the best analyses which have been made of the remaining bases are given by M. Liebig, as follows:*

	ARICINE. Pelletier.	ATROPINE. Liebig.	CONICINE. Liebig.	CORYDALINE. Fr. Döbereiner
Carbon. . .	71.0	70.98	66.91	63.05
Hydrogen. .	7.0	7.83	12.00	6.83
Nitrogen. .	8.0	4.83	12.81	4.32
Oxygen. . .	14.0	16.36	8.28	25.80
	<hr/> 100.0	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

* Handwörterbuch der Reinen und Angewandten Chemie, b. i, 709.

	DELPHININE.	EMETINE.	NARCEINE.	
	Couërbe.	Pelletier.	Pelletier.	Couërbe.
Carbon. . .	76.69	64.57	54.73	57.02
Hydrogen. .	8.89	7.17	6.52	6.64
Nitrogen. .	5.93	4.30	4.33	4.76
Oxygen. . .	7.49	22.96	34.42	31.58
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

	PSEUDOMORPHINE.	SABADILLINE.	SOLANINE.
	Pelletier.	Couërbe.	Blanchet.
Carbon.	52.74	64.18	62.11
Hydrogen.	5.81	6.88	8.92
Nitrogen.	4.08	7.95	1.64
Oxygen.	37.37	20.99	27.33
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

	VERATRINE.		MENISPERMINE.	STAPHISAININE.
	Couërbe.	Dumas and Pellet.	Pellet and Couërbe.	Couërbe.
Carbon. . .	71.48	66.75	71.89	53.57
Hydrogen. .	7.67	8.54	8.01	8.71
Nitrogen. .	5.43	5.04	9.57	5.78
Oxygen. . .	16.42	19.60	10.53	11.94
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

MORPHIA AND THE OTHER BASES IN OPIUM.

When incisions are made in the heads of the white poppy, (*Papaver somniferum*) a milky juice exudes, which is allowed to dry by evaporation on the plant, then scraped off and collected, it forms opium. This drug has been minutely examined, and several vegetable bases derived from it. Its narcotic and anodyne properties are chiefly due to morphine, which is also the base that opium contains in largest proportion.

Morphine or morphia, $C_{35}H_{20}NO_6$.—Much soluble matter is extracted from opium when treated repeatedly in a divided state with water. Most of the narcotine, however remains in the residuum, from which it may be extracted by dilute hydrochloric acid, or by boiling alcohol or ether. If the

aqueous solution be greatly concentrated by evaporation, and mixed with a strictly neutral solution of chloride of calcium, a brown impure precipitate of meconate of lime is thrown down, while the bases are converted into hydrochlorates. The liquid being filtered may be made distinctly acid with hydrochloric acid, then digested, in order to discolour it, with pure animal charcoal previously deprived of all phosphate of lime by an acid, filtered again and evaporated for crystallization. A radiated crystalline mass is deposited which consists of hydrochlorate of morphine in combination with hydrochlorate of codeine. This mass may be drained and expressed, then dissolved in hot water, and precipitated by ammonia, which throws down the morphine, while the codeine remains in solution. By farther concentration of the liquid an additional quantity of morphine is deposited; when afterwards an excess of caustic potash is added to the liquid, what remains of the morphine is retained in solution, and the codeine precipitated. Thebaine, narcotine, &c., remain in the former brown mother-liquor, which afforded the crystallized double salt of hydrochlorate of morphine and codeine.

Morphine may be prepared, without reference to the other bases in opium, by various processes, of which the following appears to be the best. The opium is macerated thrice in succession, each time with three parts of cold water, and the mass after each digestion strongly expressed. The liquids are united, raised to the boiling point, and mixed with an equal bulk of milk of lime, the latter containing a quantity of hydrate of lime equal to about one fourth of the weight of the dry opium employed. After boiling for a few minutes the mixture is strained through linen; all the narcotine, meconic acid, &c., remain in the lime precipitate, while all the morphine is contained in the solution in combination with lime. This solution is greatly concentrated by evaporation, then filtered, heated to the boiling point and pounded sal ammoniac is thrown into it, in about the proportion of 1 ounce of sal ammoniac to 1 pound of opium. The caustic lime is thus converted into chloride of calcium, the morphine loses its solvent, and is precipitated in small crystalline needles. Opium yields upon an average a sixteenth of its weight of morphine. (Mohr.)

Morphine as precipitated by ammonia forms a white pulve-

rulent mass, but when crystallized from alcohol it assumes the form of small colourless brilliant prisms. It requires 1000 times its weight of water to dissolve it, but tastes sensibly bitter, and has an alkaline action. Morphine is scarcely soluble in ether, but dissolves in 40 times its weight of cold and in 30 times its weight of boiling alcohol; it is very soluble in caustic alkali. It is fusible by heat, with the loss of water of crystallization, and on solidifying again forms a crystalline mass. Morphine and its salts strike a deep blue colour with the solution of a persalt of iron made as nearly neutral as possible; they likewise decompose iodic acid and liberate iodine, which may then be detected by solution of starch.

Hydrochlorate of morphine crystallizes in needles or feathery crystals, which require from 15 to 20 times their weight of cold water to dissolve them, but dissolve in less than their own weight of boiling water. This, which is perhaps the most valuable of the salts of morphine for medical use, is prepared directly from opium.* *Sulphate* of morphine is highly soluble, and crystallizes like the hydrochlorate. *Bisulphate* of morphine has been formed. *Acetate* of morphine crystallizes with difficulty and is apt to lose a portion of its acid even when kept in crystals; it is much employed in medicine. *Bimeconate* of morphine is a crystallizable salt, in which one of the three atoms of water of meconic acid, is replaced by morphine; this salt also is prepared for medical use; morphine is supposed to exist in opium in combination with meconic acid. The latter acid can easily be detected by re-agents (page 937); and being found in no other vegetable matter but opium, meconic acid is the substance looked for in testing for opium, of which it is an infallible index.

2. *Narcotine*, $C_{48}H_{24}NO_{15}$, the first crystalline substance derived from opium, is remarkable for its solubility in ether, by means of which it may be dissolved out of opium. It forms colourless brilliant prisms, is tasteless, insoluble in water and caustic alkali, soluble in alcohol. Its solution has no alkaline reaction, but narcotine dissolves in acids; its salts do not crystallize.

3. *Codeine*, $C_{35}H_{20}NO_5$, is remarkable for its solubility in water, being soluble in about 2 parts of boiling water, also in

* By the process invented by Dr. Robertson and improved by Dr. W. Gregory; Edinburgh Medical and Surgical Journal, Nos. 107 and 111, also Jour. de Phar., xix. 156.

alcohol and ether. It has a weak taste, alkaline reaction, and fuses by the heat of boiling water.

4. *Thebaine* or *paramorphine*, $C_{25}H_{14}NO_3$, is crystallizable, has an alkaline reaction and sharp taste.

5. *Narceine*, a weak base which exists in opium in a very small proportion. Two other bases, *pseudomorphine* and *porphyroxine* have been discovered in certain species of opium. Opium also contains a neutral substance *meconine* in minute quantity, of which the elements are carbon, oxygen and hydrogen only.

QUININE AND CINCHONINE.

Peruvian bark owes its febrifuge qualities to these bases, which it contains in combination with tannic and kinic acids. Quinine is most abundant in *yellow bark*, usually considered as the bark of the *Cinchona cardifolia*, while cinchonine prevails in the grey bark considered as the bark of the *Cinchona nitida* or of the *Cinchona condaminea*.

The ground bark is boiled in water acidulated with hydrochloric acid, the filtered solution mixed with an excess of milk of lime, the precipitate washed, expressed and dried. From this precipitate, which contains quinine, cinchonine, tannate of lime and other matters, the two bases are dissolved out by boiling alcohol; the solution which is strongly coloured is filtered, neutralised with dilute sulphuric acid and the alcohol distilled off. Sulphate of quinine crystallizes on cooling, and is obtained colourless by treatment with animal charcoal and repeated crystallization. The sulphate of cinchonine may be obtained from the coloured mother liquor. Both bases may be isolated by precipitating a solution of their salts in water, by means of ammonia. (Wöhler.)

Quinine, $C_{20}H_{12}NO_2$.—This base is precipitated by ammonia in white flocks, which are not crystalline, and is crystallized even from solution in alcohol with difficulty; but from hot alcohol containing a little ammonia quinine is deposited in fine needles. It is in the state of a hydrate, which fuses about 302° and loses the whole of its water. Quinine is very bitter, alkaline, soluble in 200 parts of boiling water, and highly soluble in alcohol. Most of the salts of this base are crystallizable, intensely bitter and are precipitated by alkalis, bichloride of platinum and oxalic acid.

Subsulphate of quinine, the ordinary sulphate of quinine of the shops, crystallizes in tufts composed of fine needles, which are very light, slightly flexible and have a pearly lustre. It requires 740 parts of water to dissolve it at 55°, but only 30 parts at 212°; it is very soluble in dilute sulphuric acid. It fuses with the appearance of wax, and loses 11½ per cent or 6 atoms of water. The crystallized salt contains 2 atoms of quinine and 8 atoms of water to 1 atom of sulphuric acid. *Neutral sulphate* of quinine is formed by adding a little sulphuric acid to a solution of the sub-sulphate; it crystallizes well in rectangular prisms with rectangular or square bases, is soluble in 11 parts of water at 55°, and fuses in its water of crystallization at 212°. It reddens vegetable blues, although its taste is not perceptibly sour but strongly bitter; it contains 8HO.

Cinchonine, $C_{20}H_{12}NO$.—This base crystallizes readily from alcohol in brilliant prisms. It requires 2500 times its weight of boiling water to dissolve it, and is less soluble in cold water. It is but slightly soluble in cold ether; in its other properties it resembles quinine. *Neutral sulphate* of cinchonine crystallizes also in large octohedral crystals of a rhomboidal base, having a mother of pearl lustre; it contains 8 atoms of water.

STRYCHNINE AND BRUCINE.

These alkalies are derived from the *Nux vomica* class of plants and particularly from the seeds of *Strychnos nux vomica*, and St. Ignatius' bean, the fruit of *Strychnos ignatia*. To extract them, powdered *nux vomica* is boiled repeatedly in water, the infusion is concentrated to a syrup and mixed with hydrate of lime in the proportion of 2 ounces of quicklime to 1 pound of the *nux vomica*. The two bases are contained in the insoluble portion of the mass, which is dried and exposed to boiling alcohol. On evaporating the alcoholic solution strychnine crystallizes first, while the brucine and a portion of strychnine remain in the mother liquor. To complete the separation, the bases in the mother liquor are neutralised by greatly diluted nitric acid, and the nitrate of strychnine crystallized out, while the salt of brucine remains still in solution being much later of crystallizing. From the salts, purified as

usual by animal charcoal, and dissolved in water, the bases may be precipitated by ammonia.

Strychnine or *strychnia*, $C_{44}H_{23}N_2O_4$; as obtained from the evaporation of its alcoholic solution it assumes the form of minute colourless octohedrons, composed of two four-sided pyramids, between which a four-sided prism is sometimes interposed. It is soluble in 2500 parts of boiling and in 6667 parts of cold water; but the last solution, weak as it is, has an intensely bitter taste. It is insoluble in absolute alcohol and ether, but sensibly soluble in aqueous alcohol; not fusible. Strychnine acts with great energy on the animal economy, inducing tetanus. Its poisonous action is best counteracted by an infusion of gallnuts or warm tea. The salts of strychnine are generally crystallizable.

Brucine, $C_{44}H_{25}N_2O_7$.—This alkali was first discovered in 1819 by Pelletier and Caventou in the bark of *Brucia antidysenterica*. Brucine greatly resembles strychnine in its properties, acts in the same way on the animal economy but is much less poisonous. It is more soluble in water, and is strongly reddened by nitric acid, while pure strychnine is not.

VERATRINE.

This alkali is found in the seeds of different species of *Veratrum*, particularly of *Veratrum album* or white hellebore, and *Veratrum sabadilla*, in which it exists combined with veratric acid, (page 955). It is extracted by a process similar to that for strychnine. Veratrine has the aspect of a resin, is friable and gives a white powder; it cannot be crystallized. It is nearly insoluble in water, but dissolves in alcohol and ether. Its taste is excessively acrid and not bitter; with sulphuric acid it becomes yellow, red, and at last violet. Veratrine occasions violent irritation in any mucous membrane to which it is applied, and is highly poisonous. Few of its salts except the hydrochlorate and sulphate are crystallizable; they are not precipitated by bichloride of platinum.

Sabadilline is a crystallizable base which accompanies veratrine in the seeds of *Veratrum sabadilla*. *Jervine* is another base found in the root of *Veratrum album*.

CONICINE.

This base is also termed *conia* and *coneine*; its formula is $C_{12}H_{14}NO$. It exists in all parts of hemlock, *Conium maculatum*. It is volatile and is obtained by the distillation of the plant or its seed with a solution of caustic alkali, in the manner formerly indicated. It is a colourless oily liquid, of density 0.89, boiling at 302° ; its odour is strong and penetrating, recalling at once that of hemlock and tobacco. The taste of conicine is acrid and corrosive, and it occasions death almost as rapidly as hydrocyanic acid. It is soluble in 100 parts of water, alkaline, miscible with alcohol and ether. With sulphuric, phosphoric, nitric and oxalic acids it forms salts, which crystallize well. Solutions of both conicine and its salts undergo decomposition when air is admitted to them, and become brown with formation of ammonia.

The following organic bases are well established, besides those already enumerated :

Aconitine, in several species of aconitum.

Aricine, in a variety of cinchona bark.

Atropine, in all parts of *Atropa belladonna*. This base is soluble in water, and is readily decomposed when in solution by heat; it crystallizes in small white prisms. Its taste is most disagreeably bitter and acrid. In a state of solution, and particularly when in combination with acids, it is easily decomposed with the formation of ammonia. It is highly poisonous, and in the most minute proportion possesses the power to dilate the pupil of the eye. The formula for atropine is $C_{34}H_8NO_6$.

Chelidonine and *chelerythrine* in *Chelidonium majus*.

Colchicine in *Colchicum autumnale*.

Corydaline in the root of *Corydalis bulbosa* and *fabacea*.

Curarine in the Curara poison of India.

Daturine in the seeds particularly of *Datura stramonium*.

Delphinine in the seeds of *Delphinium staphisagria*.

Emetine in *ipecacuanha*, the root of *Cephaelis ipec*. It is a white, very fusible powder of a feebly bitter taste, sparingly soluble in water, readily soluble in alcohol; it excites vomiting.

Hyoscyamine in *Hyoscyamus niger* and *albus*.

Nicotine exists in the leaves and seed of different species of tobacco, namely *Nicotiana tabacum* and *Nicotiana rustica*. It is soluble in water, has the consistence of butter and distils at 284° .

Pelosine in the root of *Cissampelos pareira*.

Solanine in several species of *Solanum*, and in the first shoots of germinating potatoes.

The following bases are not so well known and still problematical: apirine, azaridine, blanchinine, buxine, carapine, castine, chioccine, crotonine, cynapine, daphnine, digitaline, esenbeckine, eupatorine, euphorbiine, fumarine, glancine, glaucopirine, jamaicine, menispermine, paramenispermine, pitayine, sanguinarine, staphisaine, surinamine, violine. Besides two bases in *Carthagen* quinquina bark and in chinova bark. (Liebig.)

CHAPTER X.

CYANOGEN AND ITS COMPOUNDS.

Cyanogen, $\text{NC}_2=\text{Cy}$, which, when free, is a gas (page 428), is remarkable as an organic radical, and enters as a constituent into a large class of compounds. It combines directly with hydrogen, forming a hydrogen-acid, with the whole of the metals forming salts, and is also obtained in combination with oxygen forming several acids, and with chlorine. Cyanogen also appears to be a constituent of urea and uric acid, and of the numerous bodies derived from the decomposition of the latter.

Formation of cyanogen.—This compound is always primarily obtained as a constituent of ferrocyanide of potassium (page 450). In order to explain the reaction between animal matters and carbonate of potash, when fused together at a red heat, which gives rise to that salt, it is necessary to keep in mind the following properties of the salt:—When heated to redness in a close vessel, ferrocyanide of potassium is decomposed into cyanide of potassium, carburet of iron and nitrogen gas; that is,

looking upon the ferrocyanide of potassium as a double cyanide, the cyanide of iron is converted into carburet of iron and nitrogen gas, while the cyanide of potassium escapes decomposition. The cyanides of metals in general which can combine with carbon, are decomposed in the same way as the cyanide of iron; thus the cyanide of silver when heated gives at first a little cyanogen, but afterwards it fuses, and glowing suddenly, gives nitrogen gas, the carbon remaining in combination with the silver. The addition of carbonate of potash to the heated ferrocyanide of potassium prevents the decomposition of any cyanogen, cyanide of potassium being then formed, together with oxide of iron; and when charcoal forms a third ingredient of the fused mixture, the oxide of iron is reduced to the metallic state. Hence ferrocyanide of potassium cannot be supposed ready formed in the red-hot mixture of the iron pot in which it is manufactured, that mixture containing both charcoal and carbonate of potash.

In the manufacture of this salt, animal substances, such as dried blood, horn, hoofs, and bristles, with common pearlashes, are the materials employed. The animal matter is used either in its natural state, or it is previously submitted to distillation, as in the preparation of ammonia, and the residual charcoal merely employed for the manufacture of the prussiate. The projection of animal matter into the melted potash occasions a lively effervescence, from the evolution of carbonic acid and some combustible gases. The liquid is stirred after each addition of the materials. The usual proportions employed are equal parts of pearlashes and animal matter, or ten parts of the former and eight parts of carbonised animal matter. Three or four per cent of iron filings are usually added to the mixture. After each addition of animal matter the heat is urged until the whole is fused, and the melted material, which is of a thick consistence, is not removed from the pot until the charcoal is seen to be equally diffused through the whole mass. The mass, after cooling, is placed in an iron pan filled with water, the clear liquid after a time drawn off, and water boiled several times on the insoluble residue. The liquids are evaporated for crystallizing the salt at a temperature not exceeding 203° Fahr. The formation of prussiate takes place after the solution of the

melted mass, by the action of the matters dissolved upon the insoluble residue; for this melted mass yields nothing but cyanide of potassium to alcohol, and contains no prussiate. In explanation of the formation of cyanide of potassium in the melted mass, it is stated by Liebig that metallic potassium readily produces that salt when fused with calcined blood, disengaging at the same time a considerable quantity of charcoal; the proportion of nitrogen to carbon, in cyanogen, being one equivalent of the first to two of the last, while in blood, hair, and horn, the proportion is 1 to 6. Now when these animal matters are fused at a high temperature with potash, the free charcoal reduces the potash to the state of potassium; the latter then acts upon the azotised carbonaceous matter, forming cyanogen, with which it unites. A second mode in which cyanide of potassium is produced, is when ammoniacal gas is conducted over a mixture of carbonate of potash and charcoal at a red heat. This is accounted for by the action of ammonia upon charcoal alone at a red heat; the gas is entirely converted into hydrocyanic acid and hydrogen (NH_3 and $2\text{C}=\text{H}, \text{NC}_2$ and 2H). Now hydrocyanic acid decomposes carbonate of potash at a red heat, forming cyanide of potassium. Hence the product of cyanide of potassium is most considerable when the animal matter is used in its natural state, and not previously carbonised, a fact of which the manufacturers of prussiate of potash have long been aware from experience. To account for the subsequent conversion of the cyanide of potassium in the process into prussiate, it is absolutely necessary that iron exist in the fused mass; but it may indifferently be in the condition of metallic iron, the protosulphuret or the protoxide of iron. The first is readily dissolved by a solution of cyanide of potassium with evolution of hydrogen gas (3KC_y with HO and $\text{Fe} = 2\text{KC}_y, \text{FeC}_y$ and KO and H); the second with the formation of sulphuret of potassium, and the third with that of caustic potash. When the iron is added in the state of protosulphate to a solution of cyanide of potassium, one third of the latter salt becomes cyanide of iron (a brown insoluble matter), which is dissolved by the other two-thirds of the alkaline cyanide, and the ferrocyanide formed. These processes are not altered in the slightest degree by mixing caustic potash or its carbonate, or the sulphuret of potassium, with the solution of cyanide of

potassium. Much of the iron necessary is derived from the corrosion of the iron pot in which the fusion is conducted.*

HYDROCYANIC ACID.

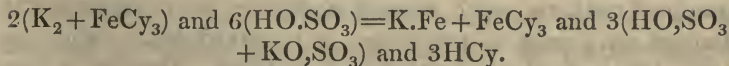
Syn. *Prussic acid* formula, $H + Cy$. This acid was discovered by Scheele, and its constitution first ascertained by Gay-Lussac. It may be obtained anhydrous by transmitting dry sulphuretted hydrogen gas over cyanide of mercury in powder, and contained in a glass tube; sulphuret of mercury being formed, and hydrocyanic acid liberated. The vapour of the latter should be carefully condensed, by conducting it into a Liebig's condenser charged with ice-cold water. It may also be obtained very conveniently by the following process of M. Trautwein. Fifteen parts of ferrocyanide of potassium (page 450) are distilled in a glass retort, at a very gentle heat, with 9 parts of sulphuric acid previously diluted with 9 parts of water and cooled, and the product conducted into a well cooled condenser, containing 5 parts of chloride of calcium in coarse fragments. The distillation is stopt as soon as the salt in the condenser is entirely covered by fluid; and the latter is poured off and transferred into a bottle with a well ground stopper, and secluded from light.

Hydrocyanic acid is a colourless liquid, of density 0.6967 at 64° , still liquid when free from water at -64° , boiling at 80° ; miscible with water, alcohol and ether in all proportions. It consists in the state of vapour of 2 volumes of cyanogen and 2 volumes of hydrogen united without condensation; its combining measure is therefore 4 volumes, like that of all other hydrogen-acids; and its theoretical density 943.7, air being 1000. It has a peculiar, very penetrating and suffocating odour, resembling that of the distilled water of bitter almonds, its taste is very bitter and burning. Hydrocyanic acid is in the highest degree poisonous, and its vapour when inspired, produces immediately fatal effects. Its poisonous action is best counteracted by the inhalation of air containing chlorine or ammonia. Hydrocyanic acid scarcely reddens litmus; its vapour is very inflammable. When pure it easily undergoes decomposition,

* Liebig; Proceedings of the Chem. Soc. of London, vol. i. p. 2.

particularly under the influence of light, ammonia being formed with a brown precipitate. This decomposition is prevented by a slight admixture of any other acid. When potassium is heated in the vapour of hydrocyanic acid, cyanide of potassium is formed, and the hydrogen of the acid is disengaged as gas. When its vapour is passed over ignited quicklime or barytes, a mixture of cyanide of the metal and cyanate of its oxide is formed, and pure hydrogen disengaged. Chlorine decomposes hydrocyanic acid, and forms hydrochloric acid and chloride of cyanogen.

The aqueous solution of hydrocyanic acid may be prepared by precipitating potash from cyanide of potassium, by means of tartaric acid, and may in this way be obtained at once of a determinate strength and in a good condition for preservation (page 452). But to prepare this acid in considerable quantity the following process may be followed, which is that of Geiger with the proportions modified. Eight parts of ferrocyanide of potassium with 7 parts of oil of vitriol diluted with 36 parts of water, are slowly distilled nearly to dryness, the product being transmitted through a Liebig's condenser, and collected in a receiver containing at first 8 parts of water. The condensed liquid contains very uniformly 1.62 parts of hydrocyanic acid, which corresponds with one half of the quantity of cyanogen in the salt, the other half of the cyanogen remaining in the residuary insoluble ferrocyanide; the latter is white or yellowish-white when pure, but is often coloured by prussian blue. In this reaction 2 equivalents of ferrocyanide of potassium are decomposed by 6 equivalents of sulphuric acid, which liberate 3 equivalents of hydrocyanic acid. The residuary products are an insoluble ferrocyanide of potassium and iron, $K, Fe + FeCy_3$ (Everitt), and 3 equivalents of bisulphate of potash; or:



If ferrocyanide of potassium be viewed as a double cyanide of iron and potassium, $FeCy + 2KCy$, then the decomposition in the foregoing process is limited to the cyanide of potassium of the salt, of which cyanide 3 atoms are decomposed out of

the four contained in 2 equivalents of the double salt; and the residuary insoluble double cyanide is $2\text{FeCy} + \text{KCy}$.

The proportion of hydrocyanic acid in the acid prepared by the preceding process may be ascertained by accurately weighing a portion of it, amounting to about 100 grains; adding to this portion nitrate of silver in excess, collecting the white insoluble precipitate of cyanide of silver which falls on a weighed filter, drying and weighing together precipitate and filter. Five parts of the precipitate correspond to 1 part of hydrocyanic acid. Or red oxide of mercury may be used to test the strength of the aqueous acid. A drop or two of caustic potash is added to a weighed quantity of the dilute acid, and then a known weight of the red oxide of mercury in fine powder is agitated with it. The metallic oxide dissolves readily as cyanide of mercury, every 4 parts of oxide dissolved corresponding with 1 of anhydrous acid. The hydrocyanic acid may then be reduced to any degree of strength desired, by the addition of water.

The dilute acid, when absolutely pure, soon decomposes, becoming brown and then black, but has stability imparted to it by the smallest trace of sulphuric acid; an addition which should be made when it is intended to preserve hydrocyanic acid for medical use. The solution has the taste, odour and poisonous qualities of the anhydrous acid.

Hydrocyanic acid may be detected by its odour, or by adding a few drops of sulphuric acid to the liquid containing it, and covering the vessel with a glass plate having its lower surface moistened by a solution of nitrate of silver. The hydrocyanic acid rises from its volatility, and produces a white precipitate in the nitrate of silver.

But the most delicate and satisfactory indication of hydrocyanic acid is the production of Prussian blue from it, by a process which is known as Scheele's test. If the liquid to be examined contains much organic matter, as the contents of the stomach in a case of poisoning, it is mixed with about one sixth of its bulk of oil of vitriol and distilled. The test is then applied to the distilled liquid.

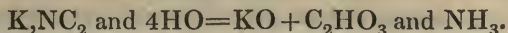
1. A few drops of protosulphate of iron are added to the liquid to be tested, with a slight excess of caustic potash so as to precipitate the oxide of iron.

2. The alkaline liquid, after a few minutes' exposure to air,

to allow of the formation of some peroxide of iron, is made acid by the addition of hydrochloric acid, when Prussian blue is formed and precipitates.

Hydrocyanic acid does not decompose carbonates, and may therefore be purified from other acids by distilling it from chalk. But the acid so distilled cannot be preserved without adding a trace of a mineral acid to it.

Cyanides.—Hydrocyanic acid forms a metallic cyanide and water with red oxide of mercury, oxide of silver and other metallic oxides of which the metal has a feeble affinity for oxygen. The cyanides of these metals are not decomposed by dilute oxygen-acids, and resist for a long time the action of concentrated and boiling nitric acid. But the same cyanides are decomposed very easily by sulphuretted hydrogen and hydrochloric acid. The cyanide of mercury is resolved when heated into metal and cyanogen, a portion of the latter remaining in the retort as *paracyanogen*, a black coaly matter, isomeric with cyanogen. Caustic potash is not neutralised by hydrocyanic acid, but remains strongly alkaline, while the solution retains the odour of the acid. Hence it is doubted whether cyanide of potassium is then formed, and rather supposed that hydrocyanic acid unites directly with oxide of potassium. But the solid cyanide of potassium, when dissolved in water, has the same characters as the preceding solution. Cyanide of potassium dissolves the metallic cyanides insoluble in water, forming double salts, and then acquires stability. Cyanide of potassium is decomposed when heated with a solution of caustic potash; the cyanogen of the former salt, uniting with the elements of water, is converted into formic acid and ammonia:



The insoluble cyanides of all the non-alkaline metals may be obtained by adding hydrocyanic acid to an acetate of the metal.

DOUBLE CYANIDES.

The soluble cyanides of potassium and sodium dissolve all the insoluble cyanides of the metals proper, and form double com-

pounds, generally crystallizable, which are not decomposed or modified by alkaline carbonates nor metallic chlorides.

Protocyanide of iron, FeCy , with certain other cyanides, comports itself in a peculiar manner with other metallic cyanides and also with hydrocyanic acid. The cyanide named in combination with two equivalents of cyanide of potassium, $\text{FeCy} + 2\text{KCy}$, forms a neutral salt, *ferrocyanide of potassium*, (page 450), which is not poisonous, gives no hydrocyanic acid with sulphuric acid at the ordinary temperature, while its iron is not precipitated by an alkali or alkaline carbonate; or in this compound the properties of both a cyanide and salt of iron entirely disappear. If the potash of this double salt is precipitated by tartaric acid, a new double cyanide is formed, highly acid and crystallizable, containing protocyanide of iron with 2 equivalents of hydrocyanic acid, $\text{FeCy} + 2\text{HCy}$, known as *ferro-cyanic acid*, or *ferrocyanide of hydrogen*. On the view of the constitution of these salts proposed by M. Liebig, they contain a bibasic salt-radical ferrocyanogen FeCy_3 , in combination, with 2K in the first, and with 2H in the second. Ferrocyanide of lead, $2\text{Pb}, \text{FeCy}_3$, is a white precipitate with a shade of yellow, formed on adding ferrocyanide of potassium to a salt of lead. Ferrocyanide of copper, $\text{Cu}_2, \text{FeCy}_3$, a reddish brown precipitate, insoluble in dilute acids, formed on adding ferrocyanide of potassium to a salt of black oxide of copper. Sesquiferrocyanide of iron or *Prussian blue*, $\text{Fe}_4, 3\text{FeCy}_3$, is precipitated on adding the same soluble ferrocyanide to a persalt of iron (page 564). With a protosalt of iron, a greenish white precipitate is produced, which according to Berzelius, is a double ferrocyanide of potassium and iron, $\text{K}, \text{Fe}_3, 2\text{FeCy}_3$ (page 557).

Sesquicyanide of iron, Fe_2Cy_3 , in combination with other cyanides, forms another class of compounds, analogous to the preceding. With 3 equivalents of cyanide of potassium, $(\text{Fe}_2\text{Cy}_3 + 3\text{KCy})$ it forms the red prussiate of potash, or ferricyanide of potassium, $\text{K}_3, \text{Fe}_2\text{Cy}_6$ (page 450). With 3 equivalents of hydrocyanic acid, $\text{Fe}_2\text{Cy}_3 + 3\text{HCy}$, it forms *ferricyanic acid* or *ferricyanide of hydrogen*, $\text{H}_3, \text{Fe}_2\text{Cy}_6$; it is obtained by decomposing the insoluble ferricyanide of lead by sulphuretted hydrogen. The ferricyanide of potassium produces with a protosalt of iron, ferricyanide of iron, $\text{Fe}_3, \text{Fe}_2\text{Cy}_6$, a beautiful variety of Prussian

blue (page 557). The same alkaline ferricyanide does not disturb a persalt of iron.

Sesquicyanide of cobalt, Co_2Cy_3 , forms with other cyanides a class of double salts strictly analogous to the immediately preceding class, and which are represented as compounds of a tribasic salt-radical, *cobalticyanogen*, Co_2Cy_6 , or as cobalticyanides. *Cobalticyanide of potassium*, $\text{K}_3\text{Co}_2\text{Cy}_6$ was discovered by L. Gmelin, and is prepared by heating slightly a mixture of protoxide of cobalt, or its carbonate, with a solution of potash supersaturated with hydrocyanic acid; hydrogen is disengaged with a slight effervescence, and the solution when evaporated, furnishes the salt in question in reddish-yellow crystals, which require to be purified by a second crystallization. It is isomorphous with ferricyanide of potassium.

Sesquicyanide of manganese, Mn_2Cy_3 , appears also to form with other cyanides a similar class of salts (page 534).

Sesquicyanide of chromium, Cr_2Cy_3 , appears to exist in a class of double cyanides of the same type.

Chromocyanide of potassium, $\text{K}_3\text{Cr}_2\text{Cy}_6$, is formed when a mixture of hydrated oxide of chromium with a solution of hydrate of potash to which an excess of hydrocyanic acid has been added, is allowed to evaporate spontaneously in air. The liquid acquires a reddish-brown colour, and deposits yellow crystals, which have a similar form and composition with ferricyanide or cobalticyanide of potassium. (Böckmann).

Bicyanide of platinum, PtCy_2 , is considered by Liebig as existing, as a radical, in a series of platinum compounds, discovered by M. Doebereiner. This salt-radical is monobasic. *Platinocyanide of potassium*, $\text{K}, \text{PtCy}_2 + 3\text{HO}$, is formed on exposing to a heat approaching redness a mixture of equal parts of platinum sponge and dried ferrocyanide of potassium. A solution of the heated mass affords first, when evaporated, crystals of ferrocyanide of potassium, and then of platinocyanide of potassium. The latter crystallizes in thin elongated rhomboidal prisms, which are blue by reflected and yellow by transmitted light. Its solution does not precipitate nitrate of lead, but nearly all the other metallic salts. *Platinocyanic acid* or *platinocyanide of hydrogen*, H, PtCy_2 is obtained by decomposing the platinocyanide of mercury suspended in water by a stream of sulphuretted hydrogen gas. It crystallizes in a confused

mass, of which the faces reflect a copper lustre ; its solution is strongly acid.

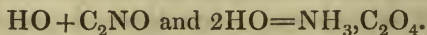
COMPOUNDS OF CYANOGEN WITH OXYGEN.

Cyanogen forms the three following isomeric acid compounds with oxygen :

Cyanic acid	. . .	HO, Cy O ,
Fulminic acid	. . .	$2\text{HO, Cy}_2\text{O}_2,$
Cyanuric acid	. . .	$3\text{HO, Cy}_3\text{O}_3.$

Cyanic acid, $\text{HO} + \text{CyO}$. This acid is formed when cyanogen gas is dissolved in a solution of caustic potash, or passed over carbonate of potash heated to redness ; also when ferrocyanide of potassium in a fine powder is ignited in a shallow iron vessel, with stirring and exposure to air at a low red heat. It does not exist except in combination. The hydrated acid was prepared by Wœhler by distilling dry cyanuric acid, and collecting the product in a receiver surrounded by ice.

It is a transparent very volatile liquid, of a pungent odour, highly corrosive, miscible with water. Soon after its preparation this liquid spontaneously undergoes a very extraordinary change ; it is converted with the evolution of heat into a white solid matter, *cyamelide*, having the same composition in 100 parts, but insoluble in water and dilute acids, dissolved by caustic alkali, with the formation of ammonia, a cyanate and cyanurate of the alkali. The probable formula of cyamelide is $\text{NH} + \text{C}_2\text{O}_2$ (Liebig). Cyanic acid in solution reddens litmus at first, but is soon transformed into bicarbonate of ammonia, by uniting with the elements of 2 atoms of water :



Cyanates.—The alkaline cyanates are soluble, all the others are insoluble. They are recognised by the decomposition of their acid, which occurs soon after it is liberated by another acid. Ammonia forms two compounds with cyanic acid ; one which contains more ammonia than belongs to a neutral salt is produced when the acid vapour and dry ammoniacal gas are

mixed together, and forms a white woolly crystalline substance. This cyanate affords ammonia when treated by an alkali, and its acid undergoes the usual decomposition when liberated by another acid. But if heated, either dry or in solution, it loses a little ammonia, still retaining, however, the elements of a neutral cyanate, and is transformed into urea, a change the more remarkable that urea is a substance belonging to the animal economy.

Urea or anormal cyanate of ammonia, $C_2O_2N_2H_4 = C_2O_2 + 2NH_2$ (Dumas). This substance, discovered by Vauquelin and Fourcroy in urine, was obtained from cyanic acid and ammonia by Wöhler, and is the first peculiarly organic product which was formed artificially. It exists in the form of lactate of urea in human urine, and combined with hippuric acid in the urine of the cow and elephant (Cap and Henry). Urea combines with most acids without neutralising them, and is a feeble base.

The following is an advantageous process for urea from human urine, without the use of alcohol. Fresh urine is evaporated in a water-bath to about $\frac{1}{12}$ or $\frac{1}{10}$ of its volume, allowed to cool and filtered. Oxalic acid is taken in the proportion of about half an ounce to each pint of urine employed, dissolved in twice its weight of hot water, and the solution slowly added with continual agitation to the concentrated urine; a large production of a buff-coloured precipitate results, which is oxalate of urea. The impure oxalate, when quite cold, is collected on a large calico filter, slightly washed with a cold solution of oxalic acid, and pressed in the hands as strongly as possible, to get rid of the mother liquor containing salts, &c. The solid mass of oxalate of urea is next dissolved in hot water in a capacious vessel, and neutralised with chalk (whiting) rubbed up with water to a thick cream. So soon as the acid reaction to test-paper ceases, the whole may be thrown on a filter to drain, and squeezed to avoid unnecessary loss. On digesting the solution with animal charcoal, again filtering and concentrating, without ebullition, to a small bulk, crystals of urea are deposited on cooling; these have a brownish colour and disagreeable smell, but by a second solution in warm water, with the addition of a little more bone-black and filtration, the substance is obtained snow-white and inodorous. The urea obtained in this manner

burns without sensible ash, and its solution is not troubled by a salt of lime. In the latter part of the evaporation of the first impure solution of urea filtered from the oxalate of lime, insoluble oxalate of lime separates in crusts upon the surface, which must be removed by filtration.

Or, nitrate of urea may be formed by adding to the concentrated urine in a shallow bason an equal bulk of nitric acid of 1.42, taking care by the gradual mixing of the acid and placing the bason in cold water, to prevent any considerable elevation of temperature. This precaution is necessary, for the urine contains chlorides, which when decomposed by the action of nitric acid and heat, produce chlorine and nitrous acid, bodies which re-act injuriously upon urea. The impure nitrate of urea which crystallizes is washed several times with dilute nitric acid, and then dried by placing it upon a clean porous brick or tile, which imbibes the acid liquor. It is redissolved and discoloured by means of animal charcoal, crystallized again, and the solution of colourless nitrate of urea treated with carbonate of barytes or carbonate of potash till perfectly neutralised. The nitrate of barytes or nitrate of potash crystallizes first from the concentrated solution at a low temperature, and the urea afterwards from the mother liquor of those crystals. The urea may be purified from any adhering salt by solution in alcohol and crystallization from that liquid.

Urea may also be prepared in large quantity by decomposing the insoluble cyanate of lead with ammonia or its carbonate.

Urea crystallizes in colourless, flattened, four-sided prisms, is soluble in its own weight of cold water, in 4 or 5 parts of cold alcohol, and in 2 parts of boiling alcohol; it fuses at 248° .

The taste of its aqueous solution is cooling, like that of nitre, acrid and bitter. It is persistent in dry air, but deliquesces in damp air. At a high temperature it undergoes decomposition and produces ammonia, cyanate of ammonia, and solid cyanuric acid. Alkalies give no indication of ammonia in a cold solution of urea, nor is cyanic acid precipitated from it by the metallic salts. The latter acid, however, is revived when a solution of urea is evaporated with nitrate of silver, cyanate of silver being deposited in a crystalline state, and nitrate of ammonia remains in solution. When urea is dissolved in fused potash or in concentrated and boiling sulphuric

acid, it assumes the elements of 2 atoms of water, and is converted into carbonic acid and ammonia.

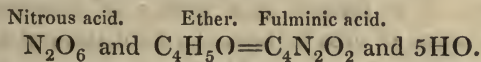
Nitrate of urea is soluble in 8 parts of cold water. It consists of single equivalents of urea, nitric acid and water. (Regnault).

Oxalate of urea crystallizes in long thin prisms, which are much less soluble in water than the nitrate, and have an acid taste. This salt also contains an atom of water. From the oxalate of urea, compounds of urea with other acids may be obtained, by precipitating the oxalic acid with a neutral salt of lime of the other acid, and thus the hippurate, lactate, sulphate, &c. have been formed and crystallized by MM. Cap and Henry.

FULMINIC ACID.

Formula of the acid supposed anhydrous: $C_4N_2O_2 = Cy_2O_2$.

Fulminic acid exists in certain fulminating compounds of silver and mercury, discovered by Mr. Howard, but its true nature was first ascertained by Gay-Lussac and Liebig. The acid is bibasic; it undergoes decomposition when separated from bases by a stronger acid, into hydrocyanic acid and other products. Fulminic acid is formed by the action of an excess of nitric acid and alcohol upon nitrate of silver or nitrate of suboxide of mercury. A variety of products result from the mutual action of nitric acid and alcohol, including nitrous acid; 2 atoms of which with 1 atom of ether are resolved, in contact with oxide of silver or mercury, into water and fulminic acid, the last combining with the metallic oxide:



Fulminate of silver is also immediately formed and precipitated on transmitting the vapour of nitrous acid through a saturated solution of nitrate of silver in alcohol.

Fulminates.—The salt of *suboxide of mercury* is prepared by dissolving 1 part of mercury in 12 parts of nitric acid of 1.36, by a gentle heat; then adding 11 parts of alcohol of 0.848, and heating by a water-bath. A violent reaction soon occurs, with

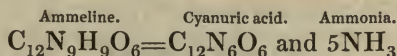
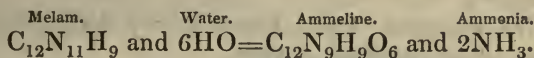
the escape of nitrous ether vapour, and precipitation of metallic mercury; and soon fulminate of mercury is deposited in white opaque granular crystals, which may be washed when cool, and dried at the ordinary temperature. This salt crystallizes from boiling water in fine, silky needles, and may thus be deprived of the free mercury with which it is accompanied. Fulminate of mercury detonates violently by percussion, or when rubbed between hard bodies; in the flame of a candle it deflagrates with a feeble explosion. Mixed intimately with 6 times its weight of saltpetre, it forms percussion powder, which is introduced in the state of a paste with water, into the copper capsules used with fire-arms. Fulminate of *silver* is prepared like the salt of mercury, but with about twice as much alcohol. It detonates even more violently by percussion than the salt of mercury, and also by heat. This fulminate is deprived of only half its base by an alkali, and a salt formed containing 1 atom of alkali and 1 atom of oxide of silver as bases. Nitric acid throws down an acid fulminate of silver, containing an atom of water as the second base; it is crystallizable and more soluble than the neutral salt. The action of hydrochloric acid upon fulminate of silver is attended with the formation of an acid containing chlorine, *chlorocyanhydric acid*, of which the probable composition is $\text{H}_2 + \text{C}_2\text{NCl}_5$ (Gay-Lussac and Liebig).

CYANURIC ACID.

Formula of the acid crystallized from water: $3\text{HO}, \text{Cy}_3\text{O}_3 + 4\text{HO}$.

Cyanuric acid was discovered by Scheele and examined by Serullas, but its true constitution was first ascertained by Liebig and Wöhler. It is formed in a variety of circumstances; in the decomposition of urea by heat, the distillation of uric acid, in the decomposition of the solid chloride of cyanogen by heat, &c. M. Liebig recommends its preparation from Melam (p. 1000). A portion of melam is gently warmed in a little strong sulphuric acid until dissolved; the acid liquid is poured into about 30 parts of water, and boiled in a flask, with the occasional addition of water for four or five days, till the liquid no longer gives a precipitate of ammelide with ammonia. By evaporation the fluid gives brown crystals of cyanuric acid, which may be made

colourless by repeated crystallization, or when this fails by dissolving in concentrated sulphuric acid and precipitating by water. The white precipitate by water gives colourless crystals of cyanuric acid from a solution in boiling water. In this process, melam on dissolving in sulphuric acid is transformed into ammonia and ammelide, and the last in contact with the acid diluted with water is resolved into ammonia and cyanuric acid, as expressed in the following equations :



Cyanuric acid has a feeble acid taste, is slightly soluble in cold water and dissolves in 24 parts of boiling water. The crystals from water are oblique prisms of a rhombic base; they contain 4HO, which they lose in air at the ordinary temperature. Cyanuric acid is obtained anhydrous and crystallized, from a concentrated and boiling solution in nitric or hydrochloric acid. One atom of cyanuric acid is decomposed by dry distillation and resolved into 3 atoms of hydrated cyanic acid, of which it contains the elements. It dissolves with the aid of heat in the concentrated mineral acids, without decomposition, but is decomposed by continued boiling with the formation of carbonic acid and ammonia.

Cyanurates.—In these salts the three atoms of water of the hydrate of cyanuric acid are replaced in whole or in part by metallic oxides. They are all completely decomposed, and their acid liberated by nitric and hydrochloric acids.

Gaseous chloride of cyanogen, CyCl, is most conveniently prepared by passing chlorine in excess into an aqueous solution of hydrocyanic acid, and expelling the chloride of cyanogen by a gentle heat. It is a gas at the ordinary temperature having an insupportable, penetrating odour, and provoking tears. At 0° Fahr., it crystallizes in long needles like spiculæ of ice. It undergoes a metamorphosis if confined liquid in a tube, and deposits the solid isomeric chloride of cyanogen (Persoz). It combines with ammonia, as $\text{CyCl} + 2\text{NH}_3$.

Solid chloride of cyanogen, Cy_3Cl_3 , corresponds in constitution with cyanuric acid; it is formed when a mixture of dry chlorine and hydrocyanic acid is exposed to the direct rays of the sun. It is white and sublimes in diaphanous needles. When digested in hot water, it is resolved into hydrochloric and cyanuric acids. It combines also with ammonia, as $\text{Cy}_3\text{Cl}_3 + 3\text{NH}_3$.

Bromide of cyanogen, CyBr , crystallizes in cubes, but is gaseous at 59° .

Iodide of cyanogen, CyI , forms snowy flocks, white and crystalline, which volatilise at 113° .

SULPHOCYANOGEN.

Its formula as it exists in combination is CyS_2 ; or it is the bisulphuret of cyanogen.

When chlorine is transmitted into a strong solution of sulphocyanide of potassium, a solid matter of a fine yellow colour is precipitated which was considered as sulphocyanogen, but has been shown, by Mr. Parnell, to be different, and named meta-sulphocyanogen. Sulphocyanogen, as it exists in the sulphocyanide has not yet been isolated.

Hydrosulphocyanic acid, $\text{H} + \text{CyS}_2$ is obtained by decomposing the basic sulphocyanide of lead by dilute sulphuric acid, and completing the decomposition by sulphuretted hydrogen. It is a colourless liquid of a sour taste, which spontaneously resolves itself in air into several products. It has not been obtained anhydrous. It colours red the solution of a persalt of iron; it is not poisonous.

Sulphocyanides.—The preparation of sulphocyanide of potassium has already been described (page 452). The neutral sulphocyanide of *lead* is deposited in yellow opaque and brilliant crystals, on mixing concentrated solutions of acetate of lead and sulphocyanide of potassium. The basic sulphocyanide, $\text{Pb,CyS}_2 + \text{PbO}$, on throwing the neutral salt into boiling water, or on adding the tribasic acetate of lead to sulphocyanide of potassium. It is a yellowish white crystalline powder, insoluble in water.

PRODUCTS OF THE DECOMPOSITION OF SULPHOCYANOGEN.

Metasulphocyanogen, $C_{12}N_6S_{12}H_3O$ (Parnell). This is the yellow substance precipitated by the action of chlorine on sulphocyanide of potassium in solution, with formation of chloride of potassium. It is also formed by the action of nitric acid upon the same salt. Metasulphocyanogen dissolves entirely in a solution of caustic potash. An acid added to this solution throws down a lemon yellow precipitate, with a small quantity of a black matter, which has not been fully examined. The yellow substance is the *hydrothiocyanic acid* of Mr. Parnell, of which the probable formula is $C_{10}N_5S_{12}H_6O_2 = H_4Cy_5S_{12} + 2HO$. The neutral thiocyanides contain 4 atoms of metal in the place of H_4 , and when insoluble are yellow, while the thiocyanides combined with metallic oxide are black.*

Mellon, C_6N_4 (page 428). This is the fixed residue which remains as a yellow powder, on heating dry metasulphocyanogen to low redness in a glass flask, sulphur and bisulphuret of carbon being volatilised at the same time. It was discovered by M. Liebig, who supposed 4 atoms of sulphocyanogen ($C_8N_4S_8$) to be resolved into 1 atom of mellon (C_6N_4) 4 atoms of sulphur ($4S$) and 2 atoms of bisulphuret of carbon (C_2S_4). But Mr. Parnell has observed the appearance in the decomposition of metasulphocyanogen, of water, sulphuretted hydrogen, and hydrosulphocyanic acid, in addition to the products above. He supposes three equivalents of metasulphocyanogen to be resolved into four of mellon, $C_{24}N_{16}$; two of hydrosulphocyanic acid, $S_4C_4N_2H_2$; four of sulphuretted hydrogen H_4S_4 ; eight of bisulphuret of carbon, C_8S_{16} ; twelve of sulphur S_{12} , and three of water H_3O_3 .

Mellon is insoluble in water, alcohol, and dilute acids; is decomposed at a bright red heat into three volumes of cyanogen and 1 volume of nitrogen. It is a salt-radical, combining directly with potassium, with ignition and formation of *mellonide of potassium*; with hydrogen it forms *hydromellonic acid*.

Cyanilic acid, $C_6N_3H_3O_6$ (Liebig). Mellon is decomposed by the prolonged action of boiling nitric acid, with disengagement of

* Philosoph. Mag. 3rd. Series, vol. 17, p. 249.

gas, and the liquid yields on evaporation, colourless, anhydrous octohedrons of cyanilic acid, which has the same composition as cyanuric acid, and also crystallizes from water with 4HO. The nitric acid after its action on mellon contains ammonia; it is the only acid which causes mellon to undergo this transformation.

Boiling potash ley dissolves mellon with evolution of ammonia and formation of a salt in white needles, which has not been sufficiently examined.

Hydro-persulphocyanic acid, CyS_3H (Woskresensky;) a yellow matter insoluble in water, formed when sulphocyanide of potassium heated to fusion is exposed to a stream of dry hydrochloric acid. It is soluble in boiling alcohol.

Melam, $\text{C}_{12}\text{N}_{11}\text{H}_9$ (Liebig), one of the products of the decomposition by heat of sulphocyanide of ammonium. It is most conveniently prepared by heating a mixture of dry sulphocyanide of potassium with twice its weight of sal ammoniac in a porcelain bason, above 350° or 400° , by a charcoal chauffer. Ammonia, sulphuretted hydrogen and bisulphuret of carbon go off, and melam remains mixed with chloride of potassium, from which it may be separated by washing with pure water. Melam is a greyish white powder, not crystalline, insoluble in water, alcohol, and ether. It is decomposed by heat into mellon and ammonia.

Melamine, $\text{C}_6\text{N}_6\text{H}_6$ (Liebig); a salifiable base formed by dissolving melam in 1 part of hydrate of potash dissolved in 20 parts of water; the mixture being kept in ebullition till the turbid liquor becomes perfectly clear. One atom of melam with 2 atoms of water are then resolved into 1 atom of melamine and 1 atom of ammeline. Melamine is deposited from the concentrated solution on cooling in anhydrous rhomboidal octohedrons, transparent, colourless or tinged slightly yellow. It is very slightly soluble in cold water, dissolves to a greater extent in boiling water, but its solution is very slowly effected; it is neutral to test paper, insoluble in alcohol and ether. When dry melamine is strongly heated, the greater portion of it sublimes without decomposition. Melamine forms crystallizable salts on combining with dilute acids.

Ammeline, $\text{C}_6\text{N}_5\text{H}_5\text{O}_2$ (Liebig). The alkaline solution above, from which melamine crystallizes, still contains ammeline dis-

solved in caustic potash, from which it is obtained, on neutralising with acetic acid, as a gelatinous white precipitate, this is washed and then redissolved in dilute nitric acid; the solution gives by evaporation crystals of pure nitrate of ammeline, from which, dissolved in water, pure ammeline is precipitated by carbonate of ammonia. It may also be obtained by dissolving melam in dilute and boiling hydrochloric acid.

Ammeline forms very fine brilliant silky needles; is insoluble in water, alcohol, and ether, but dissolves in caustic alkalis. Ammeline is a feeble base and combines only with the more powerful acids. Its salts are crystalline, have an acid reaction, and water precipitates ammeline from them.

Ammelide, $C_{12}N_9H_9O_6$ (Liebig), is a product of the decomposition of melam, melamine, and ammeline by concentrated acids. The solution is treated with alcohol, and the precipitate of ammelide washed with cold water. It may be purified by solution in nitric acid and precipitation by carbonate of ammonia. It is a white powder insoluble in water, alcohol, and ether; soluble in alkalis and the stronger acids. It forms a crystalline compound with nitric acid, which is decomposed by water. When long boiled in dilute nitric or sulphuric acid, ammelide is completely decomposed and converted into ammonia and cyanuric acid.

Hydrosulphurets of cyanogen.—Dry sulphuretted hydrogen and cyanogen do not combine when mixed together over mercury, but if a drop of water is added, the gases are condensed in the water, which affords thin yellow crystals by evaporation, observed by Gay-Lussac, of which the composition is $C_4N_2H_3S_3$; or an allantoin, in which the oxygen is replaced by sulphur (Vœlckel). When a stream of sulphuretted hydrogen is conducted into an alcoholic solution of cyanogen, the liquid soon becomes yellow, and deposits fine orange red crystals, when artificially cooled, discovered by Wœhler, of which the composition is $C_2NHS + HS$; its compound with lead $C_2NHS + PbS$ (Vœlckel).

Sulphocyanhydric acid and sulphuretted hydrogen.—A compound acid of these acids was obtained by Zeise, as one of the products of the reaction between gaseous ammonia and the bisulphuret of carbon in alcohol. Its empirical formula is CyS_3H_2 .

URIC ACID AND THE PRODUCTS OF ITS DECOMPOSITION.

These form a well defined class of compounds, which appear from their analysis to contain cyanogen and carbonic oxide. M. Liebig connects the different members of the class by supposing them to contain a compound radical in common, *urile*, which is itself a combination of 2 atoms of cyanogen and 4 atoms of carbonic oxide. Uric acid, $2\text{Cy} + 4\text{CO} = \text{C}_8\text{N}_2\text{O}_4$, being indicated by Ul, then the compounds are represented by the formulæ:—

Rational formulæ.		Empirical formulæ.
$2\text{Ul} + 1 \text{ atom urea}$	= Uric acid	$= \text{C}_{10}\text{N}_4\text{H}_4\text{O}_6$
$2\text{Ul} + \text{O}_2 + 4\text{HO}$	= Alloxan	$= \text{C}_8\text{N}_2\text{H}_4\text{O}_{10}$
$2\text{Ul} + \text{O} + 5\text{HO}$	= Alloxantin	$= \text{C}_8\text{N}_2\text{H}_5\text{O}_{10}$
$2\text{Ul} + 1 \text{ atom ammonia} + 2\text{HO}$	= Uramile	$= \text{C}_8\text{N}_3\text{H}_5\text{O}_6$

URIC ACID.

Formula, $\text{C}_{10}\text{N}_4\text{H}_4\text{O}_6$, or $2\text{Ul} + (\text{C}_2\text{O}_2 + 2\text{NH}_2)$. An acid which exists in the urine of all carnivorous animals, and forms the basis of most urinary concretions. It forms in combination with ammonia, the white part of the excrement of birds; and vast accumulations of that urate exist in the *guano*, or decomposed excrement of aquatic birds, by which many of the small islands on the coast of Peru and Chili are covered, and which is used as manure.

Uric acid is conveniently prepared from the chalk-like excrement of serpents. The solid urine of the Boa is reduced to fine powder and added to a boiling and very dilute solution of potash, sufficient only for the solution of a portion, and ebullition continued until the undissolved mass appears quite white.

The whole is then allowed to cool, thrown upon a calico filter, and washed until the water passes off very nearly colourless. The washed white mass, which consists of urate of potash, is next dissolved in another portion of caustic alkali, filtered, and slowly added to an excess of dilute hydrochloric acid maintained in a state of ebullition. The uric acid which precipitates, may be washed first by decantation, and afterwards more completely

on a filter, and is obtained perfectly white. From the brown liquid filtered from the urate of potash, an additional quantity of uric acid may be obtained by supersaturation with hydrochloric acid, but the product has a brownish colour.

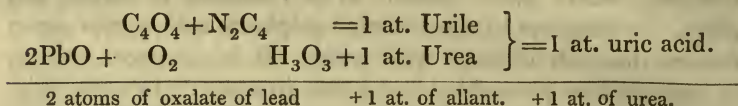
Uric acid crystallizes in thin scales of a silky lustre and brilliant whiteness, is inodorous and insipid, loses nothing at 212° . This acid is nearly insoluble in cold water, requiring, according to Prout 10,000 parts of water at 60° for solution, and but slightly soluble in hot water; its solution has a feeble reddening effect upon litmus. It is insoluble in alcohol and ether. It dissolves in concentrated sulphuric acid, and is again thrown down on dilution with water. It is also more soluble in concentrated hydrochloric acid than in water. In nitric acid, uric acid dissolves with lively effervescence, the gases disengaged being carbonic acid and nitrogen in equal volumes. The solution contains alloxan, alloxantin, urea, parabanic acid and ammonia. The concentrated liquor becomes of a purple red (from murexide), when an excess of ammonia is added, affording a character by which uric acid may be recognised. (Liebig).

Urates.—Metallic oxides appear to combine with uric acid without displacing the basic water of the acid which remains in the salt. The urates of the alkalies and alkaline earths are sparingly soluble in cold, but more freely soluble in boiling water. Urate of ammonia dissolves, according to Dr. Prout, in 480 parts of water at 60° . Urate of potash forms crystalline scales soluble in about 500 parts of cold water, but is much more soluble in boiling water, especially if there be an excess of alkali present. All the urates are decomposed by acetic acid. Urate of soda forms the principal constituent of gouty concretions.

ALLANTOIN.

Formula: $C_4H_3N_2O_3$, or $Cy_2 + 3HO$ (Liebig and Wœhler). This is a crystalline substance found in the allantoic fluid of the cow, and produced artificially by boiling uric acid with the puce-coloured oxide (peroxide) of lead. It is deposited from the allantoic fluid of the cow when concentrated by a gentle heat to one-fourth of its bulk, upon cooling, in crystals, which are treated with animal charcoal and obtained perfectly pure.

In the artificial process for allantoin, 1 part of uric acid is boiled in 2 parts of water, and the puce oxide of lead added in small qualities so long as it changes colour. The liquid, filtered boiling, and concentrated by evaporation, deposits allantoin in crystals, which are purified by repeated crystallizations. In the formation of allantoin, 2 atoms of the puce oxide of lead lose the half of their oxygen, which, with 3 atoms of water, produces 2 atoms of oxalic acid, 1 atom of allantoin and 1 atom of urea :



Allantoin crystallizes in brilliant colourless prisms derived from a rhombohedron. It is tasteless, neutral to test paper, soluble in 160 parts of cold and in less boiling water. It dissolves in nitric acid; the solution is decomposed by ebullition, without the disengagement of ruddy fumes. It also dissolves in a hot solution of an alkali or alkaline carbonate, and crystallizes from these solutions without change. Allantoin contains the elements of anhydrous oxalate of ammonia, minus 3 atoms of water, which explains its conversion by boiling alkalies into oxalic acid and ammonia. A solution of allantoin in water at the boiling temperature, to which a few drops of ammonia is added, gives a white precipitate with nitrate of silver, of which the composition is expressed by $\text{C}_8\text{N}_4\text{H}_5\text{O}_5 + \text{AgO}$ that is, 2 atoms of allantoin, $\text{C}_8\text{N}_4\text{H}_6\text{O}_6$, in which 1 atom of water is replaced by 1 atom of oxide of silver. Allantoin has also been named allantoic acid.

ALLOXAN.

Formula, $\text{C}_8\text{N}_2\text{H}_4\text{O}_{10}$. It is the erythric acid of Brugnatelli, and was discovered by Liebig and Wœhler in the decomposition of uric acid.

They recommend for its preparation, to add uric acid gradually to nitric acid of 1.35, by which it is dissolved with effervescence. "The action must be gentle, and, if heat be applied, it must be done cautiously. As soon as crystals begin

to appear in the warm liquid, no more uric acid is added for the present, and the whole is allowed to cool, when it becomes semi-solid from the separation of crystals of alloxan. The mass is thrown on a funnel stopped with a little asbestos, and, when it has ceased to drop, the acid liquor remaining in the crystals is carefully displaced by a little ice-cold water. The crystals are purified by solution in water, avoiding a strong heat, and by recrystallization. The acid liquid which has drained from the first crystals is again treated as above with uric acid, and in this way one portion of nitric acid may be made to yield 4 to 5 drops of crystals of alloxan. The mother-liquor finally left is not lost but yields a large quantity of parabanic acid, oxalurate of ammonia, or murexide, if properly treated. By this process Gregory obtains, from 100 parts of uric acid, 65 parts of anhydrous alloxan equal to at least 90 of the hydrated crystals." (Turner's Elem. of Chem. by Liebig and Gregory).

Alloxan crystallizes in large colourless octohedrons of a rhombic base, having considerable lustre; they contain 6 atoms of water and are efflorescent. A saturated hot solution gives alloxan on cooling in oblique rhomboidal prisms, which are anhydrous. It is very soluble in water, reddens vegetable colours and stains the epidermis purple. It is converted by the action of acids into alloxanic acid, and when boiled with an alkali, it is transformed into urea and mesoxalic acid. The puce oxide of lead changes it, with the aid of heat, into urea and carbonate of lead, mixed with some traces of oxalate of lead. It is transformed into alloxantin by sulphuretted hydrogen, by protochloride of tin, or by metallic zinc with hydrochloric acid. An excess of ammonia transforms it into mycomelinic acid, nitric acid into parabanic acid, sulphuric acid or hydrochloric acid into alloxantin, sulphurous acid and ammonia into thionurate of ammonia, alloxantin and ammonia into murexide (Liebig).

Alloxanic acid (supposed anhydrous), $C_4N_2HO_4$; is produced by the metamorphosis of alloxan by caustic alkalies. The anhydrous acid contains the elements of half an atom of alloxan minus 1 atom of water.

Mesoxalic acid (hydrated), $4HO + C_6O_9H$; or rather, $2HO + C_3O_4$, is one of the products of boiling a saturated solution of alloxanate of barytes or strontian. Also, when a solution of

alloxan is poured drop by drop into a boiling solution of acetate of lead, a granular very heavy precipitate of mesoxalate of lead falls, while nothing remains in the acid liquor but the excess of acetate of lead and pure urea. Both this and the preceding acid may be separated and crystallized, and are powerful acids.

Mycomelinic acid, $C_{16}N_8H_{10}O_{10}$, is formed on adding an excess of ammonia to a solution of alloxan, and raising the mixture to the boiling point. It is almost insoluble in cold water, and is thrown down as a yellow gelatinous precipitate, which becomes a yellow porous powder on drying.

Parabanic acid, $2HO + C_6N_2O_4$, is one of the products of the decomposition of uric acid or alloxan by nitric acid, discovered by Liebig and Wöhler. It is prepared by dissolving 1 part of uric acid or alloxan in 8 parts of nitric acid of ordinary strength, evaporating the liquor to a syrup, and allowing it to crystallize.

It forms thin, transparent, six-sided prisms, of a very sour taste, resembling that of oxalic acid. It is very soluble in water and does not effloresce in the atmosphere nor by heat; it is partially volatile.

Oxaluric acid, $HO + C_6N_2H_3O_7$, is formed on adding ammonia to a boiling solution of parabanic acid, or on supersaturating with ammonia a solution recently prepared of uric acid in nitric acid, which yields by evaporation crystals of oxalurate of ammonia. The acid when separated is a brilliant white powder, light and crystalline; its taste is very sour, and it reddens litmus. Its aqueous solution is decomposed completely by ebullition, and resolved into oxalic acid and oxalate of urea. It is formed by the combination of the elements of parabanic acid with 2 atoms of water. The crystallized acid contains the elements of 2 atoms of oxalic acid and of 1 atom of urea, and may be considered as uric acid in which the urile is replaced by oxalic acid. (Liebig).

Thionuric acid, $HO + C_8N_3H_5O_6(S_2O_6)$, is a bibasic acid produced by the simultaneous action of sulphurous acid and ammonia upon alloxan. Liberated from thionurate of lead by sulphuretted hydrogen, it crystallizes in very thin needles, is persistent in air, very soluble in water, and has an acid taste. It contains the elements of 1 atom of alloxan, 1 atom of ammonia and 2 atoms of sulphurous acid. On heating thionuric acid, 2 atoms of oxygen of the alloxan re-unite with 2 atoms of

sulphurous acid to form sulphuric acid, while the elements of urile, ammonia and water combine and give rise to uramile.

Uramile, $C_8N_3H_5O_6$, is prepared by adding hydrochloric acid to a saturated and boiling solution of thionurate of ammonia, till it is strongly acid; the heat is continued till the liquid begins to become turbid; it is then allowed to cool for crystallization. Uramile crystallizes in thin and hard tufts, or presents itself in the form of a brilliant white powder, composed of very thin silky needles. It is sparingly soluble in hot water, wholly insoluble in cold water, dissolves in ammonia and caustic alkalis, and is again precipitated, without alteration, by acids. A solution of potash and dilute acids boiled upon uramile, convert it into uramilic acid, disengaging ammonia. The ammoniacal solution of uramile becomes purple-red in air, and deposits crystalline needles of a green colour and metallic lustre. In contact with oxide of mercury or oxide of silver, it is decomposed, by ebullition, into murexide, and at the same time reduces the oxides to the metallic state.

Uramilic acid, $C_{16}N_5H_{10}O_{15}$, is prepared by dissolving thionurate of ammonia in cold water, adding to the saturated solution a small quantity of sulphuric acid, and evaporating by a water-bath; after a time uramilic acid is deposited in transparent, four-sided prisms of a vitreous lustre, or in silky needles. It is soluble in 6 or 8 parts of cold water, and in 3 parts of boiling water; the solution is feebly acid. In the formation of uramilic acid 2 atoms of uramile unite with the elements of 3 atoms of water, yielding up at the same time the elements of 1 atom of ammonia.

ALLOXANTIN.

Formula: $C_8N_2H_5O_{10}$. Alloxantin was first observed by Dr. Prout among the products of the decomposition of uric acid by nitric acid, and more lately produced and studied by MM. Liebig and Wœhler. Several processes are given by the latter chemists for its preparation. 1. *From uric acid*.—One part of uric acid is boiled with 32 parts of water, and dilute nitric acid added by small portions at a time till the uric acid is completely dissolved, and the liquor evaporated to two-thirds. In the course of a few days, or sometimes a few hours, the alloxantin

is deposited in crystals, which are purified by new crystallizations. 2. *From alloxan*.—It is produced in large quantity by carrying a stream of sulphuretted hydrogen into a solution of alloxan. Sulphur is first deposited, and then the whole becomes a thick mass of crystals of alloxantin, which are separated from sulphur by solution in boiling water. The alloxantin crystallizes by evaporation in a state of purity. 3. On exposing a solution of alloxan to the action of the voltaic battery, oxygen is evolved at the zincoïd, and alloxantin is deposited on the chloroid in crystalline crusts.

Alloxantin crystallizes in oblique prisms of four sides, which are colourless or slightly yellow, hard and easily reduced to powder; they become red in air impregnated with ammonia and acquire a green metallic lustre. They are not altered at 212° , but at 302° (150° centig.) lose three atoms of water; are sparingly soluble in cold water, more soluble in boiling water; the solution reddens litmus. Alloxantin heated in chlorine-water, or in strong nitric acid, is changed into alloxan; with salts of silver, it produces a black precipitate of metallic silver. It is decomposed by alkalies; barytes-water produces in its solution a violet precipitate, which is made colourless by heat, and in the end disappears entirely. By the action of boiling sulphuric acid, 2 atoms of alloxan are converted, with the concurrence of 2 atoms of water, into 1 atom of alloxantin, 3 atoms of oxalic acid, 2 atoms of ammonia, and 2 atoms of carbonic acid.

The circumstances of the formation of alloxantin are thus explained by M. Liebig. By the action of nitric acid, the urile of the uric acid combines with 1 atom of oxygen and with the elements of 5 atoms of water, giving rise to 1 atom of alloxantin and to peroxide of nitrogen, NO_4 , which in contact with water is converted into nitrous and nitric acids; the nitrous acid is decomposed with half of the urea set at liberty, while the other half of the urea forms with nitric acid, nitrate of urea. In the process again with sulphuretted hydrogen, 1 atom of oxygen of the alloxan combines with hydrogen from the sulphuretted hydrogen to form water which remains in the constitution of the alloxantin; the sulphur set free is deposited.

Products of the decomposition of alloxantin.—When a stream of sulphuretted hydrogen is carried into a boiling solution of

alloxantin, more sulphur is deposited, and on saturating with ammonia a salt crystallizes in thin colourless needles, of which the formula is $C_8N_3H_7O_8$, which is considered a compound of a new acid, *dialuric acid*, with ammonia. This acid is resolved into new products when liberated by another acid, one of these produced by exposure to air and evaporation of the solution of the ammoniacal salt in dilute sulphuric or hydrochloric acid, is *dimorphous alloxantin*, a body having the same composition as alloxantin but a different form. On mingling boiling solutions of sal ammoniac and alloxantin, the mixture becomes suddenly of a purple red colour, then gradually loses its colour, becoming turbid, and deposits colourless brilliant plates of uramile, which become rose-red on drying. The liquid contains, after its decomposition, alloxan and free hydrochloric acid. When a solution of alloxantin is heated with caustic ammonia, uramile and mycomelinate of ammonia are first formed, but are decomposed into other products by the prolonged action of ammonia and air. A recent solution of alloxantin in ammonia gradually absorbs oxygen from the air, and deposits crystals of oxalurate of ammonia.

MUREXIDE.

Formula: $C_{12}N_5H_6O_8$ (Liebig and Wöehler). This beautiful product of the decomposition of uric acid was first described by Dr. Prout, under the name of purpurate of ammonia. Murexide may be formed by evaporating a solution of uric acid in dilute nitric acid, until the solution acquires a flesh red colour, allowing it to cool to 160° , and then treating it with a dilute solution of ammonia, till the presence of free ammonia is remarked by the odour; the liquid is then diluted with half its volume of water and allowed to cool. It may also be formed by bringing together many of the products of the action of nitric acid on uric acid, with ammonia, with or without the presence of atmospheric air. The following method, proposed by Liebig and slightly modified by Gregory, appears to be the easiest and most certain, and also most productive.

“Seven grains of hydrated alloxan and 4 grains of alloxantin are dissolved by boiling in 240 grains of water, and the boiling solution added to 80 grains by measure of a cold and strong

solution of carbonate of ammonia. This mixture has precisely the proper temperature, and deposits very fine crystals of murexide. The experiment is not so successful on a large scale, probably because the liquid, by remaining longer warm, undergoes a partial change. It is best to try first a saturated solution in cold water of carbonate of ammonia. If it do not yield good crystals, add a little water, and try it again, and so on till a solution of the carbonate is obtained, which gives a good result. The difficulty is owing to the spontaneous formation of different carbonates by the action of water on the carbonate of the shops; but when a proper solution is obtained, the experiment never fails." (Turner's Chem. &c. p. 776).

Murexide crystallizes in short four-sided prisms, of which two faces, like the upper wings of cantharides, reflect a green metallic lustre. The crystals are garnet-red by transmitted light; their powder is reddish brown, and acquires a green lustre under the burnisher. Murexide is but slightly soluble in cold water, but colours it of a magnificent purple; it dissolves, however, readily in water at 158° , and crystallizes again on the cooling of its solution; it is insoluble in alcohol, ether, or in water saturated with carbonate of ammonia. But this substance cannot be purified or obtained in crystals of large size, by crystallizing it from boiling water. For on boiling murexide in a small quantity of water for the time necessary to dissolve the whole, the crystals become colourless, and upon cooling, a yellow gelatinous matter precipitates. Hence, probably, the slight uncertainty which attends even the best process for the preparation of this substance. Murexide dissolves in solution of potash, producing a superb indigo blue colour, which disappears with the application of heat, ammonia being disengaged. All the inorganic acids decompose murexide, precipitating from its solution murexan in small brilliant plates. Sulphuretted hydrogen decomposes it immediately into alloxantin, dialuric acid and murexan, while sulphur is set free.

Murexan, $C_6N_2H_4O_5$, was named purpuric acid by Prout. It is formed on dissolving murexide with heat in caustic potash, heating till the blue colour disappears, and then adding an excess of dilute sulphuric acid. It crystallizes in colourless plates, which have a silky lustre and are very brilliant, is insoluble in water and dilute acids; it dissolves in ammonia and

other alkalies, in the cold, without neutralising them. The properties of murexan closely resemble those of uramile. Like uramile, murexan boiled with water, red oxide of mercury and a little ammonia, yields murexide. The composition of murexan and uramile, also, not differing much in 100 parts, Dr. Gregory admits it to be possible that these two substances may be essentially the same.

CHAPTER XI.

SECTION I.

ORGANIC PROCESSES OF PLANTS AND ANIMALS.

Without describing the structure of the organs of plants and animals, I may state shortly the principal observations which have been made respecting the food of plants and animals and the chemical changes which it undergoes in the animal economy, with the relation which subsists between plants and animals. Besides secreting the lignin and cellulose which form the basis of their own solid structure, plants elaborate in their organs various substances destitute of structure, such as sugar, starch, gum, resins, essences, fat oils, and the endless variety of principles which the vegetable kingdom presents to the chemist for examination. These principles are either contained in the fluids of the plant, or are stored up in particular organs, or are thrown off as excretions.

The mode of formation of such principles in the plant and the chemical agencies by which one principle is transformed into another, have hitherto been very imperfectly traced, owing to the difficulty of the investigation occasioned both by the minuteness of the mechanism and the obscure nature of the decomposing forces which appear to preside in organic changes. These forces, so far as we can judge, are chiefly of the catalytic class, the azotised albuminous principles of plants having specially the function of ferments, which react generally upon other principles in the same manner, it may be supposed, as we observe diastase to operate during the germination of seeds in converting their starch into gum and sugar. Nature appears to have produced and placed near each principle its pe-

cular ferment, to effect the conversion of the former into new substances at the proper season. But the action of ferments is a department of chemistry still in its infancy.

Food of Plants.—With the exception of the provision for the first growth of the young plant which exists in its seed, the food of plants appear to be exclusively inorganic. M. Liebig has ably shown that the *humus* or decayed vegetable matter which exists in soils is not absorbed and assimilated by plants—the extremely sparing solubility of that substance being manifestly incompatible with its absorption in any considerable quantity, while even if humus did enter plants, the presumption is that like a solution of gum or sugar absorbed by the roots, it would pass through the plants unchanged, and be excreted by the leaves. The admitted value of humus in soil appears to depend almost exclusively upon its decomposition by the atmosphere, which is greatly assisted by tillage, and the formation of carbonic acid, which gas dissolved in water is taken up by the spongioles of the roots, and supplies the plant with carbon.

The ultimate constituents of all plants are oxygen and hydrogen, carbon, nitrogen, with a small portion of mineral acids and bases in the form of salts; and the condition in which the first mentioned substances enter the plant, adopting the conclusions of M. Liebig, are all the *hydrogen*, and most of the *oxygen*, as water, the *carbon* as carbonic acid, and the nitrogen as *ammonia*. All these matters are derived from the atmosphere.

Water, or its elements in the proportions of water, enters largely into the constitution of vegetable matter, forming 50 per cent of lignin, and an equally large proportion of the other neutral principles, starch, gum, sugar, &c. Certain hydrogenated compounds are also found in plants produced by the fixation of the hydrogen of water without its oxygen, which are employed by the plant for accessory purposes. They form the volatile oils which serve as its defence against the ravages of insects; the fixed oils, or fats, which envelope the seed, and which serve to develope heat by burning at the period of germination; and the wax with which the leaves and fruit are coated to render them impermeable to water.

Carbonic Acid is found as a constituent of air in a proportion

varying from 4 to 6 10,000ths. of its volume. Small as this quantity appears it is shown to exceed considerably in amount the whole carbon existing both in living vegetables and in the fossil state as mineral coal. The variation in the proportion of carbonic acid by night and by day, in winter and in summer is rightly judged by M. Dumas to be a simple meteorological phenomenon, depending upon this gas being brought down in rain, and absorbed and retained in largest proportion by water in the cold season. The gas is directly absorbed from the atmosphere by the leaves, and also from the humid soil by the roots of plants. Boussingault observed vine leaves in a glass vessel to absorb completely the carbonic acid from the air as fast as it was carried to them, however rapid the current through the vessel. M. Boucherie has also observed enormous quantities of carbonic acid to escape from the trunk of a tree cut when in full sap, evidently aspired from the soil by the roots. Under the deoxidating influence of light, plants decompose carbonic acid retaining its carbon for their own use, and returning its oxygen to the atmosphere. Their green leaves absorb the chemical rays of the sun so completely, as to give no image in the Daguerreotype. Plants thus possess energetic means of reduction which cannot be imitated, for chemists are ignorant of any method of decomposing carbonic acid in the cold. Plants, however, also exhale carbonic acid, particularly in the absence of light, and this has been supposed analogous to the expiration of carbonic acid by animals, and depending upon the respiration of plants. M. Liebig, however, looks upon this exhalation as entirely physical, as the escape by diffusion into air of the carbonic acid dissolved in the fluids of the plant, in the absence of the reducing light; the carbonic acid being derived by the roots from decomposing humus, and this exhalation most considerable from plants growing in a rich soil. Thus, at night, plants allow the carbonic acid to pass through them, without absorbing it.

Ammonia also finds its way into the atmosphere, being a product of the putrefactive decomposition of all azotised bodies, and is evolved from them principally in the condition of the volatile carbonate. The existence, however, of this substance in the air must be transient, as from its solubility in water, it will be brought down to the earth by every shower. It thus enters

the plant by its roots. Another source of ammonia is animal manure, particularly urine, which in a putrid state is rich in salts of ammonia. There can be little doubt that nitrogen, in the form of *nitric acid*, can also be assimilated by plants, as appears by the favourable action of nitrate of soda, nitrate of ammonia, and other nitrates upon vegetation.

According to the observations of M. Boussingault, the Jerusalem artichoke and leguminous plants generally can assimilate the *free nitrogen* of the atmosphere, to a small extent, but the cereals and other plants are entirely destitute of that power.* The quantity of nitric acid or nitrate of ammonia produced in the atmosphere by lightning, must be utterly insignificant, although some importance has been assigned to this as a source of the azotised food of plants.

Of the fixed earthy and saline constituent of plants which are derived from the soil, and are found in their ashes when burnt none is more generally necessary than the *silicate of potash*, which is produced in most soils by the gradual decomposition, under atmospheric influences of the felspathic minerals they contain, or is added in the form of the ashes of burnt wood and plants. *Earthy phosphates* are quite essential to the cereals, and are added to the soil in animal manure; hence the constant remark that the cereals, like the domestic animals naturally follow man in his migrations.

The vegetable kingdom is undoubtedly the great laboratory in which organic substances are produced, for from the substances enumerated, water, carbonic acid and ammonia, and not from any store of original matter in the soil are the principles in plants derived. The steps of the conversion of these into the organic principles in the organism of the plant escape detection, but the general character of vegetable action is of a reducing nature, such as the Sun's light favours, carbonic acid certainly and probably water being decomposed, their carbon and hydrogen retained, and their oxygen returned to the atmosphere.

Food of Animals.—The organic matters produced by plants form the food of animals; for animals produce little or no organic matter, but on the contrary destroy it. Indeed the

* Ann. de Chim. et de Phys. t. 76, p. 5 and t. 69, 353.

character of the chemical action of animals is exceedingly well defined, and the reverse of that of plants. The animal frame may be looked upon as an apparatus of combustion, in which the reduced hydrogen and carbon of plants are again oxidated as in a furnace, and returned to the atmosphere in the form of water and carbonic acid. Thus are sustained the animal heat, and the powers of locomotion of animals. While carbonic acid and nitrogen in the form of salts of ammonia are supplied to the vegetable world.

Animals require azotised food for their growth, for all the great constituents of the animal frame, such as its fibrin albumen, and casein are azotised matters; nothing indeed is found in the soft parts of the body which is not azotised, except water and fat, neither of which is organised. For the renewal of these parts, a constant supply of azotised food is also necessary. Gum, starch, and sugar, which contain no nitrogen, are incapable alone of supporting life for any considerable period, and animals fed exclusively upon the latter substances eventually succumb with all the appearances of death from starvation.

Respiration.—But elementary substances of the amylaceous class although they afford no element to the body, supply carbon to be burned in respiration, consisting as they do of carbon with oxygen and hydrogen in the proportions of water. In the lungs of the higher animals, the dark venous blood is exposed to air through a thin and humid membrane, permeable to oxygen from its solubility; that gas is absorbed by the blood, and imparts to it a fine florid red colour, and the characters of arterial blood. There is no reason to believe that any considerable oxidation occurs in the lungs although the gas is dissolved there by the blood. The latter containing free oxygen is carried by the circulation to the extreme capillaries, where the processes of secretion to which it contributes are most active, and where it will enter into combination in largest quantity. Indeed, it has been found by experiment that venous blood absorbs oxygen and becomes red and arterial, without producing the smallest trace of heat.

Carbonic acid being formed is carried by the venous blood to the lungs where it escapes, at the same time that the blood obtains oxygen from the air and is arterialised. From the

accurate observations of Professor Magnus on the gases of the blood, it appears that blood gives out from one tenth to one eighth of its bulk of gas when placed in vacuo; that the gas obtained from both arterial and venous blood contains nitrogen, oxygen and carbonic acid; but that while the oxygen in venous blood is at most from one fourth to one fifth of the volume of the carbonic acid, the oxygen in the arterial blood equals at least one third and sometimes almost half of the volume of the carbonic acid in the same blood.* The solvent power of the serum of the blood of the ox, for carbonic acid was found, by M. Scherer, to be double that of pure water; the serum dissolving twice its bulk of carbonic acid, while water dissolves only an equal bulk of that gas, at the usual temperature of the atmosphere.

The air of an easy expiration amounts to 15 or 18 cubic inches, and contains about $3\frac{1}{2}$ per cent of carbonic acid. The air of a deep expiration contains 6 or 8 per cent of that gas, and will not support the combustion of a candle. According to Mr. Coathupe, the quantity of air which passes through the lungs of a man of ordinary size, in twenty-four hours, is 266 $\frac{3}{4}$ cubic feet, of which 20 $\frac{3}{4}$ cubic feet are changed into carbonic acid.† The quantity of carbon thus thrown off daily from the system is considerable, and is found by M. Liebig to be in proportion to the animal heat evolved and exercise taken, and thus varies considerably in different individuals. The proportion of carbon expired by himself is 8 $\frac{1}{2}$ ounces daily, by a soldier 13 $\frac{1}{2}$ ounces, by prisoners in close confinement 7 ounces, and by a boy who takes considerable exercise 9 ounces. In an experiment made on a large scale, in which the quantity of carbon in the food and also in the excrements and urine of 856 soldiers was ascertained and compared, it was found that the carbon of the latter amounted only to one twenty-seventh part of the carbon of the former; and consequently twenty-six twenty-sevenths of the whole carbon in the food was converted into carbonic acid and discharged by the lungs.

When the expired air of man and birds is examined, the proportion of oxygen which has disappeared has generally been found sensibly the same as that of the carbonic acid produced; while it

* *Annales de Chimie et de Physique*, t. 65, p. 182.

† *Phil. Mag.* 3rd Ser. v. 14, p. 401.

will be remembered that oxygen is converted into carbonic acid, by the combustion of carbon, without any change of volume. Such should be the result if the oxygen absorbed in respiration is wholly consumed in oxidating carbon, as it must be when the food is purely farinaceous; such articles of diet as starch, sugar and gum containing already sufficient oxygen to convert their hydrogen into water, and requiring oxygen therefore to burn their carbon only.

According to some observations, upon which reliance may be placed, the oxygen which disappears in the respiration of man is always a little more than the volume of carbonic acid produced, which would indicate that a part of the oxygen is consumed in oxidating other principles besides carbon, such as the sulphur and phosphorus which are discharged in an oxidated state in the urine; and to a greater extent probably, in oxidating hydrogen, with formation of water. In the respiration of carnivorous animals, the proportion of oxygen which disappears, without being replaced by carbonic acid, is considerable, according to the observations of Dulong, a fact which may be connected with the decided excess of hydrogen over oxygen, in the composition of their food. Carbonic acid is also exhaled from the skin of man and other animals, as well as from the lungs. The question of the absorption of nitrogen from the air, in the respiration of animals, has been finally settled in the negative: they are incapable of assimilating that element in a free state. (Boussingault: *Ann. de Chim. &c.*, lxxi, 113, and 128). It is certain, however that nitrogen is occasionally exhaled from the lungs, in a sensible quantity, (Edwards,) and must come from the decomposition of an azotised constituent of the blood.

The fat of animals is a provision for the supply of oxidable matter in respiration, and speedily disappears in the absence of food, without a particle of it being discovered in the urine or feces. Fat is most abundant in herbivorous animals, because their supply of food from the vegetable kingdom ceases in winter, and is a provision for their sustenance during that period; on the contrary the bodies of carnivorous animals in a state of nature are entirely destitute of fat. (Liebig.)

The following theory of respiration or of the action of oxygen upon the blood, proposed by MM. Dumas and Boussingault, has a high degree of probability. Under the influence of the

oxygen absorbed, the soluble matters in the blood are supposed to be converted into lactic acid, an acid which has been observed in the blood by Mitscherlich, Boutron-Chalard and Fremy. The lactic acid itself becomes lactate of soda, and undergoing a true combustion from combination with oxygen is converted into carbonate of soda. The last salt is decomposed in its turn by a new portion of lactic acid, and the carbonic acid set free, with which the venous blood comes charged to the lungs. The conversion of farinaceous matters into lactic acid, out of the body, by the action of a special ferment, is a fact well understood; and the discharge by the urine, of salts of the organic acids, such as tartrates, acetates and citrates, in the form of alkaline carbonates, has also long been observed. The large production of lactic acid in the blood, and its conversion by oxidation into carbonic acid may therefore be admitted.

The oxidation occurring in respiration is quite sufficient to account for the *animal heat*. MM. Dulong and Depretz observed an excess of heat, in their experiments upon animals, which was ascribed by them, and by physiologists generally, to a calorific power peculiar to the animal and independant of respiration. But in these experiments it was assumed that an animal placed in a calorimeter with cold water, leaves it having exactly the temperature with which it entered; a thing absolutely impossible, as is now known. The cooling of the animal occasioned the excess of heat obtained in their experiments.

The animal frame appears thus to have eminently the character of an apparatus of combustion, by which the complex substances which are formed in the vegetable world and serve as food to animals, are converted again into simpler forms of matter, such as carbonic acid, water and other oxidated products, which are returned to the atmosphere and to the soil to become again the food of plants.*

Digestion.—The principal constituents of flesh and the animal fluids are all azotised substances, namely fibrin, albumen and

* “ To mount to the summit of Mont-Blanc, a man requires two days of twelve hours. During that time he burns on an average 300 grammes (10 ounces and 258 grains avoirdupois) of carbon or the equivalent of hydrogen. If a steam engine were employed to carry him there, it would burn from 1000 to 1200 grammes, to do the same work.”—*Leçon sur la Statique chimique des êtres organisés, professée par M. Dumas.*

casein, the last existing in milk and being the basis of cheese. Two very important conclusions have lately been drawn respecting the relations of these substances to each other, and their origin in the vegetable kingdom. The first is a deduction from the analysis of these substances by M. Mulder, which has been repeated and confirmed in the Giessen laboratory, namely, that these three substances are identical in composition.

The following are the results of M. Mulder's analyses :

	FIBRIN.	ALBUMEN.		CASEIN.
		Of eggs.	Of serum.	
Carbon . .	54.56	54.48	54.84	54.96
Nitrogen . .	15.72	15.70	15.83	15.80
Hydrogen .	6.90	7.01	7.09	7.15
Oxygen	} 22.82	22.81	22.24	22.09
Phosphorus				
Sulphur				
	<hr/> 100.	<hr/> 100.	<hr/> 100.	<hr/> 100.

The proportion of the carbon to the nitrogen in these substances is that of 8 equivalents of the former to 1 of the latter. They differ slightly in the minute quantity of phosphorus and sulphur with which they are accompanied. They all dissolve in concentrated hydrochloric acid, with the aid of heat, and the solutions kept for a time at a pretty high temperature, first assume a beautiful lilac, and then a rich violet blue colour. At this stage of the decomposition, each of the three substances re-acts in the same way with carbonate of ammonia and other re-agents. With considerably different physical properties, they appear to be modifications of a common principle, which Mulder names Protein, and expresses by $C_{40}H_{31}N_5O_{12}$; Liebig, by $C_{48}H_{36}N_6O_{14}$.

The second conclusion is the observation of M. Liebig, that animals draw these principles ready formed from the vegetable kingdom, and do not organise them. The parallel vegetable principles are vegetable fibrin, a constituent of gluten first properly distinguished by Liebig, and gluten itself, vegetable albumen, and legumin, or as it is termed by Liebig, vegetable

casein; the latter two being identical, equally in properties as in composition, with animal albumen and animal casein. This appears by the following analyses which were executed at Giessen.*

VEGETABLE FIBRIN.

	I. (Dr. H. Bence Jones.)	II. (Dr. Scherer.)	III. (Dr. Scherer.)
Carbon . .	53.83	54.603	54.603
Nitrogen . .	15.59	15.810	15.810
Hydrogen .	7.02	7.302	7.491
Oxygen	} 23.56	22.285	22.096
Sulphur			
Phosphorus			
	100.	100.	100.

VEGETABLE ALBUMEN.

	From rye. (Dr. Jones).	From wheat.	From gluten of plants.
Carbon . .	54.74	55.01	54.85
Nitrogen . .	15.85	15.92	15.88
Hydrogen .	7.77	7.23	6.98
Oxygen	} 21.64	21.84	22.39
Sulphur			
Phosphorus			
	100.	100.	100.

LEGUMIN OR VEGETABLE CASEIN.

	(Dr. Scherer.)	GLUTEN. (Dr. Jones.)
Carbon	54.138	55.22
Nitrogen	15.672	15.98
Hydrogen	7.156	7.42
Oxygen }	23.034	21.38
Sulphur }		
	100.	100.

The vegetable and corresponding animal principles are also

* Annalen der Chemie und Pharmacie, xxxix, 129.

accompanied by the same inorganic substances, in small quantity, namely magnesia, phosphoric acid, lime, iron, alkalies and sulphur. They evolve the same fœtid odour when heated, and give the same volatile products containing sulphur and phosphorus.

Animals thus obtain the constituents of their bodies from plants, if herbivorous, or from the bodies of other animals, if carnivorous, and merely assimilate organic principles without organising them. For the azotised vegetable principles take a new form in the animal organism, without any change in their chemical composition. The albumen, fibrin and casein of the animal system also admit, from the identity of their ultimate composition, of being readily converted one into the other, according as each is required in the animal economy. Animal digestion comes thus to be deprived of much of its mystery. M. Dumas has thus expressed himself, very lately, respecting that process.

“ Digestion is a simple function of absorption. The soluble matters pass into the blood, for the most part unaltered; the insoluble matters arrive in the chyle sufficiently divided to be aspired by the orifices of the chyliferous vessels. Digestion has evidently for an object to restore to the blood, a matter proper to furnish for our respiration the ten or fifteen grammes of carbon or the equivalent of hydrogen, which every individual burns per hour, and also to provide the gramme of nitrogen, which is exhaled every hour, in part by the lungs and skin, as well as by the urine. Thus, amylaceous matters are converted into gum and sugar; the saccharine matters formed are absorbed. The fat matters are divided, form an emulsion, and so pass into the vessels, to form afterwards deposits, which the blood takes up and burns, when they are required. The neutral azotised matters, the fibrin, albumen and casein, first dissolved, then precipitated, pass into the chyle highly divided or dissolved anew.

“ An animal, therefore, receives and assimilates almost untouched, the neutral azotised matters which he finds ready formed in the animals or plants upon which he lives; he receives oily substances which come from the same sources, and also amylaceous and saccharine substances of the same origin. These three orders of matters, of which the origin is always traceable

to the plant, divide themselves into products admitting of assimilation ; into fibrin, albumen, casein, and oily bodies, which serve to increase or renew the organs ; and into combustible products, sugar and the oily bodies, which are consumed in respiration. An animal thus assimilates, or destroys ready formed organic matters ; it creates nothing.”

Although the usual function of plants is to act, under the influence of the solar rays, like apparatus of reduction, in which water, carbonic acid and ammonia are decomposed, yet in some circumstances, they act differently and more like animals. In the germination of the seed, much heat is produced, with the formation of carbonic acid and water. The starch of grain in malting is observed to pass first into gum, then into sugar, and lastly to disappear, producing carbonic acid. Sugar thus seems to be the agent, by means of which plants as well as animals develop the heat they require. The fecundation of plants is always accompanied by heat, the flowers respiring and producing carbonic acid. They must, therefore, consume carbon ; and accordingly we find that the sugar in the stems of the sugarcane has entirely disappeared after the flowering and fructification are completed. The shot beet, turnip and carrot contain no longer a trace of sugar in their roots. The oils accumulated in some seeds appear to serve, like the fat of animals, to support this respiration, and to supply the heat, by their combustion, which plants require at certain periods of their growth, and for the discharge of certain functions.

The curious observation has also been made by M. Morren, that certain green animalculæ found in stagnant water, perform the usual function of the green parts of vegetables, decomposing carbonic acid and evolving oxygen, under the influence of the light of the sun. The proportion of free oxygen in the water is frequently raised, by their action from 30 to 56, or 57, or even to 61 per cent, while carbonic acid disappears in a corresponding proportion. It is in the *enchelide monad*, (of Bory,) only, and some other green animalculæ higher in the series, that this phenomenon is observed.*

*Ann. de Chim. et de Phys. 3 ser. 1. 456.

SECTION II.

MODIFICATIONS OF PROTEIN: ALBUMEN, FIBRIN, CASEIN.

ALBUMEN.

This substance forms the white of eggs, whence its name, and is the principal constituent of blood; it is also found in many fluid secretions, and in nearly all the solids of the animal body. It exists in two conditions, soluble, as it is in the animal fluids, and insoluble or coagulated, when heated to 158° .

Uncoagulated albumen may be prepared by evaporating the clear serum of blood, or white of egg, by a heat of 120° , till it dries up and forms a yellowish transparent brittle mass, like gum. This is reduced to powder, and washed successively with ether and alcohol, which dissolve out the fat, salts and other foreign matters in the serum or white of egg.

Dry albumen first swells up in water, then forms with it a glairy colourless fluid, which is nearly tasteless. At 140° the dry albumen begins to lose its transparency, and at 142° it changes into a white coherent mass, in which the albumen has passed into the insoluble condition. When dissolved in water it coagulates at 158° ; a very dilute solution, however does not become turbid till it is boiled. Albumen is thrown down from solution, in a coagulated state, by alcohol, creosote, by acids particularly nitric acid; by metaphosphoric acid, but not by the other hydrates of phosphoric acid, nor by acetic acid. The precipitates with acids are definite compounds of albumen with the latter. Coagulated albumen also forms compounds with acids, which are insoluble in an excess of the acid, but are soluble in water. Dilute hydrochloric acid precipitates albumen, the concentrated acid when heated dissolves the coagulum, of a lilac and then of a deep blue colour, as it also dissolves fibrin and casein. Albumen is precipitated from its soluble compounds with acids, by the ferrocyanide of potassium. Coagulated albumen dissolves in caustic alkalies and neutralises them; the solutions are precipitated by soluble metallic salts, and insoluble albuminates of the metals formed.

A solution of albumen in water is precipitated by acetate of

lead, and many other metallic solutions. Insoluble compounds are formed, one of which is of considerable interest, that of chloride of mercury; as albumen is had recourse to as an antidote to corrosive sublimate, the white of one egg precipitating about four grains of that salt. To form the *albuminate of chloride of mercury*, a solution of corrosive sublimate is added in excess to a solution of albumen, and the white flaky precipitate is collected on a filter and washed. It is slightly soluble in water, resembles the curd of milk and is insipid; it dissolves in a solution of common salt. Lassaigne finds that when heated it coagulates; the albumen appearing to abandon chloride of mercury, at the same time, which may afterwards be dissolved out by ether. It consists, when dried, according to the same chemist, of 93.4 parts of albumen and 6.6 parts of chloride of mercury, in 100 parts. Chloride of mercury forms a similar compound with fresh fibrin. The solution of albumen is also precipitated by an infusion of nutgalls.

Soluble albumen dissolves phosphate of lime, a salt, of which about 2 per cent may be separated from coagulated albumen by dilute hydrochloric acid. Metallic silver is blackened by albumen, which always contains sulphur, whether the albumen is soluble as in the egg and blood, or insoluble as in the hair.

FIBRIN.

This principle is contained by the living blood in a soluble state, but soon coagulates when withdrawn from the blood vessels. It forms the clot of coagulated blood, and constitutes muscular fibre. It is obtained in threads on stirring newly drawn blood with a stick; or by pressing the coagulum in a small stream of water, till it becomes colourless and consists of soft fibres. It is purified by washing it with ether, or warm anhydrous alcohol which dissolves out fat.

Fibrin affects a remarkable kind of aggregation, the globules of which it is composed, attaching themselves to each other by their ends, so as to form threads or fibres. In the humid state it possesses the characteristic softness and elasticity of the flesh of animals, and contains about three-fourths of its weight of water. It may be deprived of this water in dry air, and

then becomes a hard and brittle substance ; but, like flesh, it imbibes water again when moistened, and recovers its original softness and elasticity. It always leaves, like albumen, when burned, a portion of phosphate of lime.

Fibrin is insoluble in alcohol, ether and water. When boiled for a long time in water, particularly under pressure, its nature is altered and it becomes soluble. Coagulated albumen comport itself in the same way. Fibrin forms compounds with both acids and bases. In concentrated acetic acid it swells up and forms a transparent colourless jelly, which dissolves in a considerable quantity of boiling water. This solution is precipitated by ferrocyanide of potassium. In other concentrated acids fibrin undergoes a similar change. Fibrin dissolves in caustic alkalies and neutralises them. It is separated from them by acids, and precipitated.

The fibrin of venous blood may be entirely dissolved in a solution of nitrate of potash, although not without rubbing in a mortar and digestion in the cold for some time. The solution is coagulated by heat, and greatly resembles a solution of albumen, (Berzelius, Scherer). This solubility in nitre is not possessed by fibrin from the following sources : arterial blood, the "buffy coat," and that obtained by stirring blood, nor by fibrin after exposure for some time to the air, or fibrin boiled in water for a few minutes, or digested in alcohol. M. Scherer observes that, when in the soluble condition, fibrin is a highly alterable substance, absorbing oxygen readily and emitting carbonic acid ; but after being boiled for a few minutes it produces no carbonic acid in an atmosphere of oxygen gas. He concludes that fibrin, although always insoluble in pure water, has still an uncoagulated and coagulated condition, like albumen ; that it is uncoagulated in the clot of venous blood, and when soluble in a solution of nitre ; but coagulated as it exists in arterial blood, from the absorption, he supposes, of oxygen, and after being boiled for a few minutes, or treated with alcohol. The decomposition of peroxide of hydrogen, with evolution of oxygen gas is occasioned, he finds, by fresh fibrin from all kinds of blood, but not by boiled fibrin ; nor is the decomposition produced, it will be remembered, by coagulated albumen. A solution of venous fibrin in nitre, contained in a deep cylindrical jar, allows a precipitate in fine flocks to fall,

when the jar is open, but not when it is covered and access of air prevented. This precipitate is insoluble in the solution of nitre, and possesses the properties of arterial fibrin.*

PROTEIN.

Formula : $C_{40}H_{31}N_5O_{12} = Pr$ (Mulder). When albumen or fibrin is dissolved in a moderately strong solution of caustic potash, and heated to about 120° , the small portions of phosphorus and sulphur which it contains, are separated in the form of phosphate of potash and sulphuret of potassium; and when this solution is saturated with acetic acid, a gelatinous substance precipitates which is the same from both fibrin and albumen, and constitutes protein. After being washed, protein is still gelatinous, of a greyish colour, and semi-transparent. When dried it is yellowish, hard, easily pulverised, tasteless, insoluble in water and alcohol. Like albumen and fibrin it is not fusible by heat without decomposition.

Albumen and fibrin may be considered as compounds of protein with sulphur and phosphorus in different proportions. Mulder found in fibrin and in the albumen of eggs from 0.36 to 0.38 per cent of free sulphur, with from 0.32 to 0.43 per cent of free phosphorus, which quantities of these elements are in the proportion of $SP\frac{1}{2}$. In albumen from the serum of blood, 0.68 per cent of sulphur, and 0.33 per cent of phosphorus were found, or $S_2P\frac{1}{2}$. The composition of these substances is thus represented by Mulder :

Fibrin, and the albumen of eggs . . .	10 Pr + S $P\frac{1}{2}$
Albumen of serum	10 Pr + $S_2P\frac{1}{2}$

The oxides of lead and silver likewise combine with 10 atoms of protein. The globulin of blood, vegetable albumen, and the casein of milk, treated with alkalies, in the same way as fibrin and albumen, give also a protein which is identical in composition and properties with the foregoing.

M. Liebig has adopted for protein the formula $C_{48}H_{36}N_6O_{14}$, which is different from that of Mulder, although equally com-

* Scherer, *chemisch-physiologische Untersuchungen*. Annalen der Chemie, &c., X., October, (1841).

patible with the analytical results. It gives the composition of protein, per cent.

Carbon	55.742
Hydrogen	6.827
Nitrogen	16.143
Oxygen	21.288
							<hr/>
							100.000.

M. Dumas represents the composition of protein differently, I am not aware upon what authority, assigning to it more oxygen, than Mulder and Liebig. His formula is $C_{48}H_{35}N_6O_{17}$; which is 48 atoms of carbon with the elements of 6 atoms of ammonia and of 17 atoms of water. The combustion of protein and all its compounds is effected with difficulty in the combustion tube; to burn the carbon completely, M. Scherer found it quite necessary to mix chlorate of potash with the oxide of copper, or to burn with chromate of lead.

Protein combines with both acids and bases, and is soluble in all acids when highly diluted. In combining with acids it forms new compound acids; with sulphuric acid *sulpho-proteic acid*, $Pr + SO_3$. It combines also with $2HCl$. *Chloroproteic acid*, $Pr + ClO_3$, is formed on passing chlorine gas through a solution of albumen, and precipitates in white flocks. The same compound is formed by the action of chlorine on ammoniacal solutions of casein and fibrin (Mulder).

Xanthoproteic acid, $2HO + C_{34}H_{24}N_4O_{12}$ (Mulder), is formed when albumen, or any other protein-compound is digested in nitric acid. The albumen, &c., dissolve of a yellow colour, with escape of nitrogen gas, and the formation of oxalic acid and ammonia. Two atoms of protein, 1 of water, and 2 of nitric acid, yielding 3 of oxalic acid, 2 of ammonia and 1 of hydrated xanthoproteic acid as represented above. After being washed with boiling water, this acid forms a tasteless orange-yellow powder, which combines equally well with acids as with bases. The salts containing the last dissolve in water of a dark red colour.

Leucin, $C_{12}H_{12}NO_4$, a substance discovered by Braconnot. When boiled with caustic alkali in excess, protein or any pro-

tein-compound is completely decomposed, and ammonia, carbonic acid, formic acid, and three azotised bodies, are formed: leucin, protid and erythroprotid. The alkaline solution is neutralised with sulphuric acid, poured off from the sulphate of potash which precipitates, evaporated to dryness, and the mass boiled with alcohol. *Erythroprotid*, is first deposited, as a reddish brown extractiform mass. This substance, as it exists in combination with oxide of lead, is expressed by $C_{13}H_8NO_5$. Later, the leucin separates in a crystalline state. *Protid*, $C_{13}H_9NO_4$, which is a yellowish uncrystallizable brittle substance, remains in solution, with formiate of potash. The leucin crystallizes in brilliant plates, like cholesterin, is inodorous and tasteless, and sublimes unchanged at 338° . It is but slightly soluble in water, and still less soluble in alcohol. It is not decomposed by alkalis. It combines with 1 atom of the protohydrate of nitric acid, and becomes *nitroleucic acid*, which forms crystalline salts containing 1 atom of base, without losing its leucin. The same substance is also formed by the digestion of a protein-compound in sulphuric acid.

CASEIN.

The curd or coagulable portion of milk has been named casein and also *caseum*; it is a principle having considerable analogy to albumen, coagulable by rennet but not by a boiling temperature. Sweet milk contains its whole casein in solution, with globules of fat in a state of suspension, which last rise to the surface in the form of cream, or are separated, by agitation of the milk, in the form of butter. The milk contains also in solution a considerable quantity of lactine or sugar of milk (page 755), to which the casein stands in the relation of a ferment. The latter soon begins, probably after being affected like other ferments by the air, to convert the lactine into lactic acid (page 809). Milk thus spontaneously becomes sour in open vessels, and its casein is at the same time coagulated by combining with lactic acid (Fremy).

Casein combines with other acids, besides the lactic, and is best prepared according to Braconnot, by adding dilute sulphuric acid to skimmed milk; a white coagulum is formed, the sulphate of casein insoluble in water, which may be collected and washed upon a filter. It is afterwards digested with carbonate of lead,

which abstracts the sulphuric acid, and the casein becoming free is dissolved by the water. The solution of casein is evaporated to dryness, the dry matter reduced to powder and digested in boiling ether, to dissolve out fat; the residue of casein is afterwards dissolved again in water, and precipitated by the addition of alcohol, to separate it from other matters.

When dry, casein is yellowish like gum, insipid, and does not dissolve again readily in water. Its solution is also yellowish and somewhat viscid, and smells like boiled milk; left to itself it putrifies and smells like old cheese. It comports itself with reagents very like albumen; it is precipitated by acids, even by acetic acid which does not affect albumen. The precipitates formed are soluble in an excess of their acid, and also, it is said, in alcohol. Like albumen, casein exists both in a liquid and solid form. Its coagulation is effected by *rennet*, the inner coat of the calf's stomach, after it is well washed in hot water. Skimmed milk placed in contact with a small portion of this membrane, or mixed with an infusion of it, and heated to 90° or 100°, is thickened, and coagulates so completely that not a trace of the casein remains dissolved in the whey. This action of rennet is that of the pepsin it contains, but how the latter operates is unknown. Berzelius observed that 1 part of the membrane, washed and dried, placed in 1800 parts of skimmed milk gradually heated up to 122°, occasioned complete coagulation. The membrane taken out afterwards, washed and dried, was found to have lost 6 per cent of its weight. The coagulum, mixed with the fat or butter, in sweet milk, strongly compressed and dried, forms *cheese*. The fat may be dissolved out of the latter by ether.

Coagulated casein is insoluble or only very sparingly soluble in water. It dissolves easily in dilute warm vinegar and alkalies. Casein always leaves behind it, on incineration, a portion of phosphate of lime, which milk contains in considerable quantity. Casein contains a little sulphur but no phosphorus, in chemical combination. It belongs to the class of protein compounds, and may be considered a combination of 10 atoms of protein with 1 atom of sulphur. Its identity with vegetable legumin (page 912) has already been more than once adverted to.

When milk is heated in an open vessel, it soon becomes covered by a pellicle composed of insoluble matter. M. Scherer

finds that the pellicle is formed by the absorption of oxygen, and does not appear upon milk heated in an atmosphere of carbonic acid.

Fresh and pure blood-serum, mixed with twice its weight of distilled water, and a small quantity of a solution of caustic alkali, soon loses all alkaline reaction, and on heating to the boiling point, the coagulation of the albumen no longer occurs; but the solution when heated becomes covered by a pellicle, like milk. M. Scherer considers this as the conversion of albumen into casein, the pellicle agreeing closely in composition and properties with the pellicle from heated milk.

M. Scherer also finds soluble casein, always to leave, when burnt, a highly alkaline ash containing much lime, but in the coagulated state to leave a neutral ash. The solubility of the casein he, therefore, ascribes to its combination with an alkali, and its coagulation to the saturation of that alkali. The acid which saturates the alkali appears to be the lactic, produced by the change of the sugar of milk, under exposure to air, when the milk is heated.

SECTION III:

PEPSIN, GLOBULIN, HEMATOSIN, GELATIN, CHONDRIN.

PEPSIN.

This is a peculiar animal principle secreted by the stomach and present in the gastric juice. It is usually prepared by infusing the mucous membrane of the fourth stomach of the calf, which is known as rennet, and as obtained from this source is distinguished by the power which it possesses to coagulate milk. This property the infusion loses when boiled, indicating a relation between pepsin and albumen. The infusion, aided with a few drops of hydrochloric acid, and kept at 80 or 90°, dissolves completely portions of albumen boiled hard, of fibrin or boiled meat, in the course of from 12 to 24 hours. By means of this agent the process of animal digestion has been imitated perfectly, out of the body, by Eberle, Schwann and other physiological inquirers.

The most precise information we possess respecting the nature and production of pepsin has been obtained by M.

Wasmann, who first succeeded in isolating it; his observations were made upon the mucous membrane of the stomach of the pig, which greatly resembles that of man.* The organ which secretes the gastric juice consists of glands of a particular nature contained in the mucous membrane of a portion of the stomach. When this membrane is digested in a large quantity of water at from 86° to 95°, without being cut into pieces, but after being well washed, water extracts from it a variety of matters besides pepsin; but if this water be removed and fresh water added and the digestion continued in the cold, nothing almost dissolves now except pepsin. The operation may be continued with new portions of water till the membrane enters into putrefaction; water extracts pepsin at every repetition till at last nothing remains but a tissue, from which hydrochloric acid takes up no matter capable of dissolving hard-boiled albumen.

The solution of pepsin, thus obtained from the glandular membrane, is colourless, somewhat viscid, and is capable, if rendered acid by hydrochloric acid, of dissolving solid albumen very rapidly. It contains besides pepsin a little albumen, which can be separated from the acid solution by ferrocyanide of potassium, a salt which does not precipitate pepsin, or by heating the solution, if not very dilute, to 170°, or to 212° without boiling; the coagulated albumen is then deposited in flocks, with a little modified casein. The filtered liquid is no longer viscid, but preserves the property of dissolving solid albumen with the aid of a little hydrochloric acid. When boiled it becomes turbid again, and loses entirely the power to dissolve the albumen. For when the coagulated flocks are dissolved in acetic acid, they exert no solvent action on hard white of egg, even with the concurrence of hydrochloric acid; the solution of coagulated pepsin in acetic acid is not precipitated by ferrocyanide of potassium.

Pepsin thus appears to be a substance sparingly soluble in water. When its solution is evaporated to dryness, there remains a brown, greyish, viscid mass with the odour of glue and having the appearance of an extract. The solution of the latter in water is turbid, and still possesses a portion of the characteristic power of pepsin, but greatly reduced. On adding

* Pharmac. centr. Blatt. 1839. p. 349, 353.

to a fresh solution of pepsin 1 or 2 volumes of strong alcohol, the pepsin is precipitated in white flocks which may be collected on a filter. The alcoholic liquid filtered, gives on evaporation a brown deliquescent residue, which reddens litmus and is entirely deprived of digestive powers.

The precipitate of pepsin forms white flocks, which, upon drying on the filter, produce a grey compact mass. When moistened with water, it swells up and dissolves in a large quantity of water. It dissolves more easily in water acidulated with acetic or any other acid; this solution is not disturbed by ferrocyanide of potassium, and possesses in a high degree the power of dissolving coagulated albumen. A solution of dried pepsin in pure water is rendered turbid by ebullition, and loses its solvent power for aliments.

Many metallic salts precipitate pepsin, although not entirely, from a fresh solution of the membrane; such as protosulphate of iron, sulphate of copper, acetate of lead, chloride of mercury and protochloride of tin. Pepsin may again be separated from these precipitates by exposing them suspended in water to a stream of sulphuretted hydrogen; but a portion of the acid of the metallic salt remains in combination with the pepsin, forming a compound which has a well marked acid re-action on litmus, and possesses the solvent powers of pepsin in a high degree.

Acetate of pepsin may be obtained by decomposing the precipitate obtained with acetate of lead, by means of sulphuretted hydrogen, then evaporating the solution of pepsin with caution to a syrupy consistence, and treating it with alcohol. The acetate of pepsin remains undissolved by the alcohol, in the form of white flocks, which become a mass, on drying in the air, resembling gum. It does not attract humidity, but dissolves easily in water, with an acid reaction. A solution of the dried acetate in 60,000 times its weight of water, to which a little hydrochloric acid is added, dissolves white of egg in the course of six or eight hours. Alkalies appear to destroy the specific solvent power of pepsin.

Hydrochlorate of pepsin is obtained on precipitating the infusion of the mucous membrane by chloride of mercury, decomposing the precipitate, after being well washed, by sulphuretted hydrogen, and mixing the filtered liquid which contains the pepsin with alcohol, by which the hydrochlorate of pepsin

is left undissolved, like the acetate of pepsin. It possesses properties analagous to those of the acetate, and its solution in water dissolves coagulated albumen very rapidly. The alcoholic liquor above possesses no solvent power; when evaporated to dryness it leaves a residue which resembles an extract of meat.

In regard to the solvent power of pepsin for coagulated albumen, it was observed by M. Wasmann that a liquid which contains 1.7 thousand parts of acetate of pepsin and 6 drops of hydrochloric acid per ounce, possesses a very sensible solvent power, so that it will dissolve a thin slice of coagulated albumen in the course of 6 or 8 hours' digestion. With 12 drops of hydrochloric acid per ounce the white of egg is dissolved in 2 hours. A liquid which contains $\frac{1}{2}$ grain of acetate of pepsin and to which hydrochloric acid and white of egg are alternately added, so long as the latter dissolves, is capable of dissolving 210 grains of coagulated white of egg at a temperature between 95° and 104°. It would appear, from such experiments, that the hydrochloric acid is the true solvent, and that the action of the pepsin is limited to that of disposing the white of egg to dissolve in hydrochloric acid. The acid when alone dissolves white of egg, by ebullition, as it does under the influence of pepsin; from which it follows that pepsin replaces the effect of a high temperature which is not possible in the stomach. The same acid with pepsin dissolved blood, fibrin, meat and cheese, while the isolated acid dissolved only an insignificant quantity, at the same temperature; but when raised to the boiling point it dissolved nearly as much, and the part dissolved appeared to be of the same nature. The epidermis, horn, the elastic tissue (such as the fibrous membrane of the arteries) do not dissolve in a dilute acid containing pepsin.

M. Wasmann has remarked that the pepsin of the stomach of the pig is entirely destitute of the power to coagulate milk, although the pepsin of the stomach of the calf possesses it in a very high degree, from which he is led to suppose that the power of the latter depends upon a particular modification of pepsin, or perhaps upon another substance accompanying it, which ceases to be formed when the young animal ceases to be nourished by the milk of its mother.

HEMATOSIN.

The blood so long as it flows in the veins consists of a clear

liquid with floating globules observed by the microscope, which in the higher mammiferous animals are lenticular and circular or elliptical in form, of an orange red colour, and marked with a colourless spot in the centre, or nucleus. From these globules Berzelius derives two of the most characteristic constituents of the blood hematosin and globulin, which are both closely related to albumen. The clear liquor of the living blood, on the other hand, is composed of two principles already considered, namely fibrin and albumen.

To prepare, hematosin blood which has been freed from fibrin by stirring it well, is mixed with 6 times its bulk of a saturated solution of sulphate of soda, in which the blood globules are insoluble, and the latter collected on a filter. The dark-red gelatinous mass is boiled with alcohol, to which a little sulphuric acid has been added. The hematosin is thereby dissolved, while the globulin remains in combination with sulphuric acid, as a colourless or grey mass. The alcoholic solution while yet hot is mixed with carbonate of ammonia, and filtered from sulphate of ammonia and some globulin which precipitate. The solution is reduced to about 1-12th by distillation, whereby the hematosin remains as an insoluble pulverulent residue.

Hematosin is of a dark-brown colour, tasteless and insoluble in water, alcohol, and ether. It dissolves of a red colour in alcohol containing either an alkali or an acid. In aqueous solutions of the alkalies it dissolves of a dark blood-red colour; it is insoluble in hydrochloric acid. When burned it leaves behind a notable quantity of peroxide of iron. The analysis of hematosin gives :

		Atoms.
Carbon	65.84	44
Hydrogen	5.37	22
Nitrogen	10.40	3
Oxygen	11.75	6
Peroxide of iron . . .	6.64	1
	<hr/>	
	100,00	

M. Scherer has, however, shewn that the oxide of iron is not essential to hematosin, nor necessary to the colour of blood. The matter of the blood globules after being dried was intimately mixed in a mortar with concentrated sulphuric acid, and the

mass afterwards diluted with distilled water, and allowed to settle. The liquid above was perfectly clear and colourless, and contained sulphate of iron. The insoluble blood-mass was washed on a filter with water, so long as the washings contained iron. Boiled afterwards in alcohol, the mass coloured the spirit intensely red. On neutralising the sulphate of the colouring matter, the compound in solution, with ammonia, much albumen fell, which was dried and ignited; it left a white ash, in which not a trace of iron could be detected. The blood red solution in alcohol therefore contained no iron.

GLOBULIN.

This substance is the principal constituent of the blood globules; it is a protein compound and closely allied to albumen. But it has not been isolated, and little is known respecting it. The sulphate of globulin which remains behind in the preparation of hematosin, described above, consists of 4 atoms of protein, united with 1 atom of sulphuric acid. The nature of the matter forming the clear nucleus of the globules is still less understood, but it appears more like coagulated fibrin than anything else.

The matter of the blood globules, or the globulin and hematosin together, may be obtained by mixing blood freed from fibrin, with a solution of sulphate of soda, in which the matter of the globules is insoluble and precipitates; or by draining the serum out of the clot of blood cut into thin slices, upon folds of blotting paper, and afterwards mixing the clot with water, in which the matter of the blood globules dissolves of a brown-red colour and transparent. It is soluble in pure water, insoluble in serum. When its solution is mixed with salts of an alkaline base or with sugar, and exposed to air, it becomes of a lively red. The solution of the matter of the blood globules may be evaporated at 122° without losing its solubility; but when heated it coagulates, before its temperature rises to 181° , and precipitates insoluble. Both in its coagulated and soluble state the matter of the blood globules exhibits similar effects with reagents as albumen in the same conditions. M. Simon has lately maintained that this matter is composed of casein and hematosin, but coagulation by heat is not a property of casein.

GELATIN.

This is the basis of glue, size, and animal jelly, and is obtained by the action of boiling water upon skin, tendons, ligaments, cellular tissue, and serous membranes. These materials are dissolved almost entirely, by continued digestion in boiling water, and the solution forms a jelly on cooling. A substance is obtained from the permanent cartilages, by a similar treatment, which also gelatinizes, but is not precipitated by tannin, and differs in other respects from gelatin; the latter substance was first distinguished, as a peculiar principle, by Müller, and named chondrin. Gelatin is not found in the blood or any of the healthy fluids, nor does it exist as such in the solids, but is a product of their alteration by boiling water, as dextrin and starch-sugar are products of the alteration of starch by the same agent.

Gelatin is distinguished by its ready solubility in warm water, and property of forming a stiff jelly when it cools. As prepared from different materials, gelatin differs considerably in viscosity. Its viscosity, as prepared from skins, is inversely as their softness and flexibility. The most adhesive of its forms, *glue*, is prepared from the clippings of hides, hoofs and other refuse of the tannery. The solution is boiled, filtered above 120°, and after evaporation poured into square boxes to gelatinize. The jelly is cut into slices, and when dried in the air upon a netting takes the form of the cakes of glue. Glue is dissolved for use by a water-bath heat, after being softened by steeping in cold water. *Size*, which is less tenacious and adhesive, is prepared from parchment, fish skin and several animal membranes; *isinglass* from the entrails of several species of fish, particularly the sturgeon. The latter gelatin gives a colourless solution, which has no disagreeable taste or odour; it forms a firm jelly on cooling when dissolved in 100 times its weight of water.

Gelatin is insoluble in alcohol and ether. When burned it leaves behind a small portion of bone-earth. Its solution in water is not precipitated by alum, by neutral protosulphate of iron, by either the neutral or basic acetate of lead; all of which precipitate a solution of the chondrin of cartilage. Gelatin is readily soluble in diluted acids and alkalies. Its solution in

acetic acid is very gluey, but does not gelatinize. Gelatin is not precipitated by corrosive sublimate, which throws down albumen.

Gelatin forms a white compound with tannic acid, *tannogelatin*, which is precipitated by a strong infusion of gall-nuts, from a solution of gelatin in 5000 times its weight of water. The white flocks adhere to each on stirring, and form a soft, tenacious, and elastic mass, which is of the same composition with, and has considerable resemblance to leather. The skins of animals are tanned, after being cleaned and deprived of the cuticle and hair by lime-water, and allowed to enter into a degree of putrefaction to soften them, by submitting them to the action of infusion of oak bark, or other astringent vegetable matter, the strength of which is gradually increased until a complete combination takes place. The tannin is taken up by the skin, of which the weight is considerably increased by this treatment. In the tanning of thick sole-leather many months' digestion in the tan-pit is required, but the process has of late been considerably shortened by slightly heating the infusion of oak-bark by means of steam. The skin is greatly altered by its combination with tannic acid, losing its solubility in boiling water, and becoming nearly indestructible by atmospheric agencies; the animal matter it contains is no longer suitable for the preparation of prussiate of potash, by fusion with an alkali.

"*Tawed leather* is made by impregnating the skin duly prepared by washing in potash liquor, with a solution of alum and common salt; it is afterwards trodden in a mixture of yolk of eggs and water. The alum and salt re-act on each other so as to produce sulphate of soda and chloride of aluminum; the latter salt combines with the skin. White glove leather is thus prepared.

"*Wash leather* is another important manufacture; in this, the skin, after being prepared and softened, is imbued with oil, and afterwards subjected to a weak alkaline solution.

"*Curried leather*, is made by besmearing the skin, or leather, while yet moist, with common oil, which, as the humidity evaporates, penetrates into the pores of the skin, giving it a peculiar suppleness, and making it to a considerable extent waterproof. As familiar examples of these processes, the thick sole leather for shoes and boots is tanned; the upper leather is tanned and curried; the white leather for gloves is tawed; and

fine Turkey leather is tawed, and afterwards slightly tanned." (Aikin's chemical Dictionary, art. *Leather*, quoted in Brande's Manual).

Chlorine transmitted through a solution of gelatin throws down a white elastic substance in shreds, which smells of chlorous acid, while humid; it may be obtained in a dry state, by careful drying, and is a definite compound of unaltered gelatin with chlorous acid.

The composition of gelatin has also been examined by M. Scherer. He found isinglass, washed with ether to free it from fatty matters, to leave when burned 0.5 per cent of earthy ashes.

Tendons macerated for a short time in cold water, and afterwards boiled successively in alcohol and ether, and dried at 212°, left on being burned, 1.6 per cent of ashes. The purified tendons, analysed by combustion with chromate of lead, gave:

Carbon.	.	.	.	50.774
Hydrogen.	.	.	.	7.152
Nitrogen.	.	.	.	18.320
Oxygen.	.	.	.	23.754
				<hr/>
				100.000

This result was confirmed on repetition of the analysis. It leads to the following empirical formula for gelatin $C_{48}H_{41}N_{15}O_{18}$. M. Scherer observes that if this formula be doubled, gelatin will contain the elements of 2 atoms of protein, with 3 atoms of ammonia, and 7 atoms of oxygen.

Products of the alteration or decomposition of gelatin.—By long digestion, particularly at a temperature considerably above 212°, gelatin loses its power of gelatinizing, and when dried by evaporation forms a yellowish gummy mass, which dissolves easily in cold water.

Concentrated *sulphuric acid* dissolves gelatin, colourless. If the solution is diluted with water and boiled for a long time, gelatin sugar is obtained from it, on saturating with chalk.

A concentrated solution of *caustic alkali* when boiled with gelatin separates ammonia from it, and converts it into leucin

(page 1027.) and gelatin sugar. To separate these substances, the alkaline solution is saturated with sulphuric acid, after ammonia ceases to escape, evaporated to dryness, and the mass boiled with alcohol which dissolves out the leucin and gelatin-sugar. The alcohol being distilled off, the residue is washed with small quantities of cold alcohol at a time, by which the very soluble leucin is taken up. The residuary gelatin-sugar may then be dissolved in a larger quantity of boiling alcohol, and crystallizes by spontaneous evaporation.

Gelatin-sugar or *glycicoll*, $C_8H_7N_2O_5 + 2HO$, crystallizes in pretty large rhomboidal prisms, is colourless, inodorous, and very sweet. It fuses at 352° , but undergoes decomposition; is soluble in $4\frac{1}{2}$ parts of water, in 900 parts of spirits of wine, and insoluble in ether. The solution is precipitated by no metallic salt, nor by tannic acid. But glycicoll combines with oxide of lead, when digested upon it, and then loses two atoms of water (Mulder).

According to a late analyses by Boussingault, who does not appear, however, to have been aware of Mulder's analyses, the composition of glycicoll is $C_{16} H_{18} N_4 O_{14}$; of its compound with oxide of silver, $C_{16}H_{15}N_4O_{11} + 4 Ag O$. (Ann. de Chim., &c. 3 ser. p. 257).

Glycicoll dissolves without decomposition, in hot nitric acid; it forms a combination with that acid, $C_8H_7N_2O_5 + 2NO_5 + 4HO$, which crystallizes in colourless prisms, and forms double salts with bases. The composition of the double salt of lime, which does not deliquesce in air, is $CaO, C_8H_7N_2O_5 + 2 (CaO, NO_5)$.

CHONDRIN.

This variety of gelatin is derived from the permanent cartilages, such as those of the ribs, joints, wind pipe and nose, and cartilaginous bones before ossification, from the cornea of the eye, and also according to Müller, from bones in a state of caries. Chondrin is slowly dissolved out of these substances by boiling water.

The solution of this substance fixes on cooling, like that of gelatin, and when it becomes dry, by evaporation, has the ap-

pearance of solid glue. But it is not precipitated by tannic acid; on the other hand it gives precipitates with acetic acid, alum, acetate of lead and protosulphate of iron, which do not disturb a solution of gelatin. Chondrin leaves behind when burned above 4 per cent of bone earth. It appears also, like the protein compounds, to contain a small portion of sulphur in combination.

M. Scherer analysed this substance in its natural state, before it is altered by boiling, operating upon the rib-cartilage of young calves and the cornea. The cartilage was scraped clean by a knife, then digested in water containing some nitrate of potash in solution, to dissolve out albumen, and afterwards boiled in alcohol and ether for the extraction of fat. Dried at 212°, it left when burned 6.6 per cent of earthy ashes. The results of an analysis of this chondrin and also of that of the cornea were as follows:

	From rib-cartilage.	From the cornea.	By calculation.
Carbon.	50.895	49.522	50.745
Hydrogen.	6.962	7.097	6.904
Nitrogen.	14.908	14.399	14.692
Oxygen.	27.235	28.982	27.659
	<hr/> 100.000	<hr/> 100.000	<hr/> 100.000

From which, M. Scherer deduces the following empirical formula for chondrin, $C_{48}H_{40}N_6O_{20}$. Chondrin thus contains the elements of one atom of protein, with 4 atoms of water, and 2 atoms of oxygen.

Middle coat of the arteries.—This is a highly elastic membrane, of a yellowish white colour. Purified in the same manner as the rib cartilage, and dried at 212°, it left, when burnt, 1.7 per cent of ashes. Its analysis gave a result considerably different from that of chondrin, namely:

	I.	II.	By calculation.
Carbon.	53.750	53.393	53.91
Hydrogen.	7.079	6.973	6.96
Nitrogen.	15.360	15.360	15.60
Oxygen.	23.811	24.274	23.53
	<hr/> 100.000	<hr/> 100.000	<hr/> 100.000

The matter of the middle coat of arteries is therefore represented by $C_{48}H_{38}N_6O_{16}$; which is equivalent to 1 atom of protein plus 2 atoms of water (Scherer).

Membranous and compact horny matter.—This substance is a product of the organism not subject to reabsorption, and differs in that respect from all the others yet considered.

The *membranous horny matter* constitutes the epidermis, in particular, or outer skin, and also the epithelium in its different modes of formation. The *scaly epithelium* which forms the inner surface of the blood and lymph vessels, the inner surface of many mucous and serous sacs, &c. The *columnar epithelium* which forms the surface of the intestinal canal, as well as the surface of the passages from most glands. The *ciliated epithelium* which forms the surface of the mucous membrane of the organs of respiration, &c.

The *compact horny matter* constitutes hair, horn, nails, claws, &c.

I. M. Scherer's analysis of *membranous horny matter* was made upon the epidermis of the sole of the foot. It was first thoroughly washed with water, then boiled in alcohol and ether. Dried at 212° , and then burnt, it left 1 per cent of earthy ashes. Its composition, by two analyses, was :

	1	2
Carbon.	51.036	50.752
Hydrogen.	6.801	6.761
Nitrogen.	17.225	17.225
Oxygen. }	24.938	25.261
Sulphur. }		
	100.000	100.000

II. *Compact horny matter.*—Hair was cut into small pieces, well washed and digested in water, and finally boiled in alcohol and in ether. Hair of the beard, thus treated, and dried at 212° , left 0.72 per cent of ashes, when burned; hair of a blond colour from the head gave 0.3 per cent of ashes, the black hair of a Mexican gave 2 per cent of ashes. The substance of nails after similar preparation, gave 0.5 per cent of ashes, wool 2 per cent. Horn gave 0.7 per cent of ashes. Each of these substances was several times analysed, and the results from all were

similar, proving that they contain the same principle. Deducting the ashes, as usual, the results of one analysis of each were :

	Hair.	Horn.	Nall.	Wool.
Carbon. .	50.652	51.540	51.089	50.653
Hydrogen. .	6.769	6.799	6.824	7.029
Nitrogen. .	17.936	17.284	16.901	17.710
Oxygen. . }	24.643	24.397	25.186	24.608
Sulphur. . }				
	100.000	100.000	100.000	100.000

M. Scherer constructs the following formula to express the results of these analyses, and to exhibit the relation in composition of this class of substances to protein; compact horny matter, $C_{48}H_{39}N_7O_{17}$. This contains the elements of protein plus, 1 atom of ammonia and 3 atoms of oxygen.

Horn, hair, wool and other horny substances dissolve in the solution of caustic alkali, with disengagement of ammonia, and the formation of some acetic acid. When the alkaline solution is neutralised by acetic acid, effervescence occurs from the escape of sulphuretted hydrogen, and a substance falls, soluble in an excess of acetic acid, which possesses the properties and composition of protein. When the solution is precipitated by successive additions of acetic acid, the last additions give a yellowish white precipitate, which is different from the first.

Analyses of the protein from hair and of the other substance, gave the following results :

	Protein from hair.	Other substance from hair.
Carbon. .	55.150	53.516
Hydrogen. .	7.197	7.168
Nitrogen. .	15.727	14.801
Oxygen. .	21.926	24.515
	100.000	100.000

From the composition of the latter, it is supposed to be the same as the enveloping membrane of the albumen and inner coat of the lining membrane of the egg.

Feathers.—The material of feathers has hitherto been sup-

posed to be of the same nature as horn, but M. Scherer finds the composition of the former to be different, and to have considerable analogy to the second substance derived from hair and horny bodies, as appears by the following analysis :

	Quills.	By calculation.
Carbon . . .	52.427	52.457
Hydrogen . . .	7.213	6.958
Nitrogen . . .	17.893	17.719
Oxygen . . .	22.467	22.866
	<hr/>	<hr/>
	100.000	100.000

The composition is calculated, in the second column, from the formula $C_{48}H_{39}N_7O_{16}$. By which feathers are represented as having 1 atom of oxygen less in their composition than horn.

Pigmentum nigrum of the eye.—This matter, carefully removed by M. Scherer from the choroid by means of a hair pencil, in distilled water, was strained with the water through linen, to separate portions of membrane; the liquid with the black matter in suspension was then evaporated to dryness, and the residue boiled in alcohol and ether to purify it. It contains considerably more carbon than any of the preceding substances, as appears by the following analysis :

	Pigmentum nigrum.
Carbon	58.672
Hydrogen	5.962
Nitrogen	13.768
Oxygen	21.598
	<hr/>
	100.000

SECTION IV.

SECRETED FLUIDS SUBSERVIENT TO DIGESTION.

Saliva.—This liquid, which is secreted by the salivary glands, contains mucus and very small transparent globules, visible under microscope. It leaves, when evaporated, about 1 per cent of solid matter, consisting of mucus, several salts of pot-

ash, of which chloride of potassium is the most considerable, and a peculiar animal substance, which is named *salivary matter*. The latter is soluble in water, not coagulated by boiling nor precipitated by metallic salts. In the salivary glands and ducts of the horse and ass, concretions are sometimes found, which are principally composed of carbonate and a little phosphate of lime. The saliva of man and the sheep generally contains a trace of sulphocyanide of potassium; the saliva of the sheep contains also so much carbonate of soda as to effervesce with an acid.

Gastric juice.—The principal constituent of this fluid is the peculiar principle, pepsin (page 1030). When collected from the stomach during fasting, it is a transparent fluid, of a saline taste, which is neutral, but during the process of digestion it is distinctly acid from the presence of hydrochloric acid.

Pancreatic juice.—This fluid, secreted in the pancreas, is thrown into the duodenum, or the portion of the small intestines nearest the stomach, where it mixes with the partially digested food or *chyme*, as the latter leaves the stomach. It contains albumen in solution and also a matter like casein; its salts are nearly the same as those of the saliva; it has a distinct acid re-action. The uses of this fluid in digestion are unknown.

BILE AND BILIARY CONCRETIONS.

The bile which is contained in the gall-bladder is conveyed to the duodenum and added to the chyme in digestion. It is a greenish yellow fluid, of a peculiar sickening odour, and taste which is at first sweet, but afterwards bitter and exceedingly nauseous. It contains a great variety of substances, of which the most peculiar, which are all in a state of true solution, are bilin, fellinic acid, cholinic acid and biliverdin, according to the latest examination of this secretion, by Berzelius. Besides the acids mentioned, it contains oily acids combined in common with the others with soda, and several other fatty bodies, together with cholesterin. To which are to be added mucus, an undetermined animal matter, common salt, and the other usual salts of animal fluids. The separation of so many substances is extremely difficult, and the more so that the consti-

tuents of bile are remarkably prone to assume new forms under the influence of re-agents.

Bilin, the principal constituent of bile, may be isolated by the following processes. (a) The bile of the ox, after the separation of its mucus, is mixed with a little acetic acid, then filtered and precipitated by acetate of lead. The yellow precipitate, consisting of a combination of biliverdin, oleic and margaric acids with oxide of lead, is filtered, and the filtered liquid precipitated by a solution of the basic acetate of lead. The last precipitate, at first white, then yellow and plaster-like, contains fellinic acid in combination with a portion of the bile. Most of the bilin remains undissolved. The lead in the same solution is precipitated by sulphuretted hydrogen, and the solution remaining of bilin is evaporated carefully to dryness. The bilin so procured contains acetate of soda, and is likewise somewhat altered by the action of the free acetic acid during the evaporation. It is in this condition that bilin has been distinguished by the name of *bile-sugar* or *picromel*.

(b) Ox-bile is evaporated to perfect dryness on a water-bath, reduced to powder and digested with anhydrous ether, which dissolves out all the fatty bodies not in combination with bases. The mass is then dissolved in alcohol, by which, mucus, common salt, &c. are left undissolved. To the filtered liquid a solution of chloride of barium is added, by small portions at a time, so long as a dark green precipitate is formed. The last contains the biliverdin or colouring principle. The liquid filtered from it is then treated with barytes-water, added gradually, so long as a precipitate falls. The colour of different portions of the precipitate, as they are successively produced, is dark grey, soon becoming green, then brownish yellow, and at last yellow. It contains, besides biliverdin, an orange-coloured matter, not yet investigated, and margaric acid.

The liquid filtered from the last precipitate, after the precipitation of the free barytes it contains by carbonic acid, is evaporated to dryness, and the mass dissolved again in anhydrous alcohol, which leaves common salt and chloride of barium undissolved. Sulphuric acid mixed with an equal bulk of water, and then diluted by alcohol, is added gradually to the alcoholic solution to precipitate the bases it contains, in the form of sulphates. The liquid again filtered is mixed with freshly precipi-

tated carbonate of lead, for the purpose of combining its sulphuric acid and oily acids, and the greater proportion of the alcohol then distilled off. The liquid thus concentrated is filtered from the precipitate of lead salts, freed from lead in solution by sulphuretted hydrogen, filtered and evaporated to dryness in a water-bath. The transparent, yellow, bitter mass which remains, and which was formerly distinguished by Berzelius as *biliary matter*, is composed of bilin and fellinic acid.

The last product is dissolved in water and digested with finely pulverised oxide of lead, by which it forms a plaster-like mixture of fellinate and choline of lead, and the bilin remains undissolved. The filtered solution of bilin is evaporated to dryness; and to separate foreign matters, the mass is again dissolved in alcohol, filtered and evaporated to dryness. What remains is bilin. (Grundriss der Organischen chemie von Dr. F. Wöhler.)

Bilin is a translucent, colourless, inodorous mass, without crystallization, having a bitter and at the same time somewhat sweetish taste. It contains nitrogen, and is decomposed by heat, with the formation of ammoniacal products. Water and alcohol dissolve it in all proportions; it is insoluble in ether. Its solution in water is not precipitated by acids, chlorine or metallic salts. Bilin is a readily alterable substance; by boiling with caustic alkali, it is decomposed and resolved into cholic acid and ammonia. It is decomposed by acids into five different substances, namely ammonia, taurin, fellinic and cholinic acids, and dyslysin; a decomposition which may occur in the bile of the living body.

When bilin is dissolved and digested in dilute hydrochloric acid, an oily substance presents itself, consisting of bilin in combination with fellinic and cholinic acids, which by farther digestion changes into a resin-like mass, insoluble in water. The solution then contains sal ammoniac and taurin; while the resinous mass consists of fellinic and cholinic acids with dyslysin. The two former may be dissolved out of the resinous mass by cold alcohol.

Dyslysin remains undissolved in the last operation, as a resin-like mass. It dissolves, although with some difficulty, in boiling

alcohol, and falls again, after evaporation and cooling, as a white earthy mass. It has not been further investigated.

Taurin, $C_4H_7NO_{10}$, discovered by Demarçay, is a neutral substance which crystallizes in colourless regular six-sided prisms terminated by four or six-sided pyramids, of a weak taste; and is fusible by heat without decomposition. It is soluble in fifteen and a half times its weight of water at $53^{\circ}6$ (12° centig.); insoluble in absolute alcohol. It is dissolved without decomposition by concentrated sulphuric and nitric acids, and gives no reactions with the ordinary reagents.

Taurin may be derived directly from unprepared bile, when the latter, after precipitation of its mucus by hydrochloric acid, is boiled for a long time with an excess of the same acid; the liquid is poured off from the precipitated resinous acids, concentrated by evaporation, mixed with alcohol and set aside. The taurin crystallizes out mixed with common salt; the former is purified by solution in boiling water and crystallization. Taurin is the only one of these products that has been analysed.

Cholic acid may be prepared directly from bile, by precipitating the latter with acetate of lead, boiling the filtered solution with caustic potash, so long as ammonia escapes, and then adding acetic acid. The cholic acid separates in large white flocks, which soon assume a crystalline appearance.

Cholic acid crystallizes in fine needles, which when pressed together form a mass of a silky lustre, of which the taste is at once sharp and sweet; it is fused by heat, and burns like a fat. It is sparingly soluble in water, highly soluble in alcohol. It forms salts, with alkalies, of a sweet taste.

Fellinic acid is contained, with bilin and cholinic acid, in the plaster-like lead compound formed in the preparation of bilin, and in the alcoholic solution of the resinous mass produced by the treatment of bilin by hydrochloric acid. Its separation from cholinic acid is effected by saturating the last mentioned alcoholic solution with dilute ammonia and concentrating by evaporation: the choline of ammonia is then deposited as a hard mass, while the fellinate of ammonia remains dissolved. The addition of hydrochloric acid throws down the fellinic acid in white flocks.

After being washed and dried, fellinic acid forms a white, earthy, inodorous and bitter mass which fuses without decomposition at 212° . In boiling water it undergoes fusion and dissolves to a small extent; in alcohol it dissolves easily and the solution has the bitter taste of bile; in ether it is also soluble. Its salts of alkaline bases are soluble both in water and alcohol, but insoluble in an excess of alkali, and then precipitated as a plastic plaster-like substance. The salts of lead and barytes, which are insoluble, have the same appearance. It enters into combination with bilin, and forms in union with it a compound acid, which should be named *bilifellinic acid*.

Cholinic acid is separated from its salt of ammonia lately mentioned, by hydrochloric acid, in the form of white flocks, and becomes by aggregation, on drying, an easily pulverised mass. It is readily fused by the heat of hot water, in which it is wholly insoluble; it dissolves easily in alcohol.

Biliverdin is separated from its compound with barytes, mentioned under bilin, by digestion in dilute hydrochloric acid which dissolves the barytes. The residue of biliverdin is purified by solution in alcohol and precipitation from the latter by water. It forms a brilliant, greenish brown tasteless mass, insoluble in water, dissolving easily in an alkali, and precipitated from that solution in green flocks by an acid. It dissolves of a fine green colour in hydrochloric acid, and of a red tint in acetic acid. This principle of bile contains no nitrogen. The biliverdin of the bile of the ox appears to be identical with the chlorophyl of plants. That of carnivorous animals is different, although it may contain the same matter in combination with another substance. Such a substance appears to be the principal constituent of the yellow matter forming the concretions, found in the ox, which from the beauty and permanence of its tint is much prized by painters. These gall stones dissolve in caustic potash of a greenish brown colour, giving a solution which when over-saturated with nitric acid, becomes first green, and rapidly in succession blue, violet and red, and finally yellow.

Cholesterin, $C_{37}H_{32}O$.—This is a crystallizable substance which may be dissolved out of inspissated bile, by ether; it is also a constituent of the brain and nerves. It is contained in largest proportion by the gall stones of the human subject,

which generally consist of this substance combined with a portion of the yellow colouring matter of the bile. Cholesterin may be obtained by digesting these concretions in a solution of potash, by which the colouring matter is readily dissolved, and the cholesterin left white; or by dissolving them in boiling alcohol, in which the colouring matter is insoluble.

Cholesterin crystallizes from an alcoholic solution in colourless small plates, of a pearly lustre; is insoluble in water, tasteless, fuses at $278^{\circ}.6$ (137° centig.), and solidifies again in a crystalline condition. If strongly heated apart from air, it sublimes unchanged in a great measure, and condenses in plates. It is but sparingly soluble in cold alcohol; is not altered by caustic alkalies.

The bile appears to act as a stimulus to the intestinal canal generally and to assist in dividing the chyme into chyle and fecal matter, by combining with the latter.

Chyle.—This is the fluid absorbed by the lacteal vessels from the small intestines during the process of digestion. As drawn from the thoracic duct of a mammiferous animal, it is an opaque milky liquid, in which two kinds of globules are perceived by the microscope. This liquid has already a considerable resemblance to blood; it soon coagulates; the clot reddens in the air and contains fibrin. The serum which separates is composed, with the usual undetermined animal substances and salts, principally of albumen and fat, which last comes to the surface, and is what constitutes, without doubt, one of the two species of chyle-globules.

Excrements.—The excrements of man usually contain about 25 per cent of solid matter, which necessarily varies considerably with the nature of his food. Besides the indigestible residue of the food, it contains mucus, an undetermined extractive matter, fat, salts and the whole constituents of the bile, to which it owes its colour. From the incineration of 100 parts of dried excrements, 15 parts of ashes have been obtained, which were principally composed of the phosphates of lime and magnesia. The value of night soil as manure is ascribed chiefly to these salts, and salts of ammonia from the urine.

SECTION V.

LIQUIDS OF SEROUS AND MUCOUS SURFACES AND PURULENT MATTER.

Lymph.—The liquid which moistens the surface of cellular membrane is called lymph; it is chiefly water, but contains a sensible quantity of common salt and of albumen, and when concentrated a trace of alkali sufficient to affect test-paper.

The liquid secreted by serous membranes, such as the pericardium, pleura and peritoneum, resembles lymph, but contains so much as 7 or 8 per cent of albumen and salts, and is distinctly alkaline, from the presence of carbonate or albuminate of soda. The liquor amnios and fluid of hydatides are of the same composition. The water of dropsy contains in addition urea, and cholesterin suspended in fine plates. All these liquids become turbid or coagulate, when boiled, or upon the addition of nitric acid to them.

Mucus.—This is the liquid secreted by mucous surfaces, such as the nostrils. The mucus of the nostrils usually contains about 93 per cent of water, 5 per cent of mucus, with a trace of albumen and the usual salts. Mucus is insoluble in water, but imbibes it and swells up, so as to form a ropy liquid, as if it were dissolved. It shrinks up in concentrated acetic acid, and is not dissolved. When dry it is yellow. It dissolves in caustic alkali, and forms a thin liquid. Mucus contains nitrogen, but its composition is otherwise quite unknown.

Pus.—The matter secreted by an inflamed and ulcerated surface is named pus. From a healing sore it is a yellowish white liquid, of the consistence of cream, which consists of round opaque globules floating in a transparent liquid. It is insoluble in water, but may be diffused through it; on standing, the globules fall as a yellow sediment, and the supernatant liquid becomes clear and colourless.

Pus contains about 86 per cent of water, and 14 per cent of solid matter. It is coagulated by heat and by alcohol. There have been found, by analysis, in pus, two albuminous principles, several fatty bodies besides cholesterin, with the usual salts and undetermined extractive matters.

The matter of the corpuscles of pus considerably resembles

the globulin of blood. They are soluble in acetic acid with the exception of an exceedingly minute nucleus. The serum of pus contains albumen and another substance in larger quantity, to which the name *pyin* is applied, of which the solution in water is precipitated by alcohol, tannin, acetic acid, and most completely by alum, but not by ferrocyanide of potassium; the precipitates are insoluble in an excess of the reagents.

From *mucus* pus is distinguished by its different external characters, by the different form and smaller size of its microscopic corpuscles, by its different relations to water, and particularly by its becoming with caustic alkali, thick slimy and gelatinous, and in acetic acid assuming the appearance of an emulsion, while mucus becomes thinner with an alkali, and with acetic acid coagulates as a flocky matter which unites into a thready mass.

SECTION VI.

BLOOD, MILK, URINE.

Blood.—The constitution of the blood has already been described under the principal constituents of the clot, fibrin, hematosin and globulin, and albumen the chief constituent of the liquid portion. It is always alkaline from a salt of soda, probably the carbonate.

The following table exhibits the results of two careful analyses of human blood by M. Lecanu. (Ann. de Chim. &c. xlviii. 308.)

Human blood.				
Water.	.	.	.	780.145 785.590
Fibrin.	.	.	.	2.100 3.565
Colouring matter (hematosin and globulin).	.	.	.	133.000 119.626
Albumen.	.	.	.	65.090 69.415
Crystalline fatty matter.	.	.	.	2.430 4.300
Oily matter.	.	.	.	1.310 2.270
Extractive matter soluble in water and alcohol.	.	.	.	1.790 1.920
Albumen combined with soda.	.	.	.	1.265 2.010

Chloride of sodium.	.	.	.		
————— potassium.	.	.	.		
Carbonates	} of potash and soda.	.	.	8.370	7.304
Phosphates		.	.		
Sulphates		.	.		
Carbonates of lime and magnesia.	.	.	.		
Phosphates of lime, magnesia, and iron.	.	.	.	2.100	1.414
Peroxide of iron.	.	.	.		
Loss.	.	.	.	2.400	2.586
				<hr/>	<hr/>
				100.000	100.000

Milk.—The history of this fluid has been partly given under its characteristic constituents casein, milk-sugar, and the acids of butter. It contains from 10 to 13 per cent of solid matter, the rest is water. It is not coagulated by heat, but readily by all sour liquids and by rennet. When heated, a skin of coagulated casein forms on its surface. The butter of milk consists of margarine, oleine and butyrine (page 954).

Milk may be made to undergo the vinous fermentation, although very slowly, and only after it contains lactic acid; which acid probably converts the milk-sugar into grape-sugar before the fermentation occurs.

An excellent examination has been made by MM. O. Henry and A. Chevallier, of the comparative composition of woman's milk, the milk of the cow and ass, of which I subjoin the results. (Journal de Pharmacie XXV. 333 et 401.

ORDINARY MILK.

	Woman.	Ass.	Cow.
Cheese. . .	1.52	1.82	4.48
Butter. . .	3.55	0.11	3.13
Sugar of milk. . .	6.50	6.08	4.77
Salts (or mucous matter). . .	0.45	0.34	0.60
Water. . .	87.98	91.65	87.02
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

Urine.—This fluid is secreted by the kidneys from the arterial blood. The average density of healthy human urine is

1.0125, but it occasionally rises to 1.030; it is acid from free lactic acid. On standing it deposits a slimy mucus, and after a time, when stale, becomes alkaline from the formation of carbonate of ammonia. The latter salt is produced from the urea, which is accompanied in urine by a minute quantity of a fermenting principle, which occasions this transformation. Urine in its usual condition contains from 7 to 8 per cent of solid matter, the rest is water. Its characteristic constituents are urea (page 993) and uric acid (page 1002); the former is free or in combination with lactic acid, the last in an unknown combination.

Besides its usual saline constituents, the urine may contain in solution various bodies drawn by the kidneys from the blood. Many salts, such as nitrate of potash, ferrocyanide of potassium, pass through the circulation and are thrown off by the urine unaltered; so also are the organic acids, tartaric, oxalic, &c. when free; but the salts with alkalies of the same acids appear in the state of carbonates, and render the urine alkaline.

M. Lecanu has obtained some valuable results respecting the proportions of these substances in the urine of man, as affected by age and sex, which he deduces from a series of 120 analyses of urine.

He found that the quantity of urea passed in twenty-four hours, is in grammes (1 gramme = 15.44 grains troy) :

	Minimum	Mean	Maximum
By men.	23.155	28.0525	33.055
By women.	9.926	19.1165	28.307
By old men (84 to 86 years).	3.956	8.1105	19.116
By children of eight years.	10.478	13.4710	16.464
By children of four years.	3.710	4.5050	5.300

The quantity of uric acid discharged is, like the urea, sensibly the same for the same individual in equal times, but varies much in different individuals. This difference was found to be in the twenty-fours, 0.362 to 1.343 grammes in the male adults, 0.229 to 0.652 in the old men, 0.394 to 0.907 in the women, and 0.198 to 0.32 in the children. (*Journ. de Pharmacie*, XXV, 681 et 746).

The following analysis by Berzelius exhibits the composition of urine in its ordinary state, in 1000 parts :

Water.	933.00
Urea.	30.10
Uric acid.	1.00
Free lactic acid, lactate of ammonia, and animal matter not separable from them.	17.14
Mucus of the bladder.	0.32
Sulphate of potash.	3.71
Sulphate of soda.	3.16
Phosphate of soda.	2.94
Phosphate of ammonia.	1.65
Chloride of sodium.	4.45
Hydrochlorate of ammonia.	1.50
Earthy matters, with a trace of fluuate of lime.	1.00
Siliceous earth.	0.03

URINARY CONCRETIONS.

There are several distinct species of urinary calculi.

1. *Xanthic oxide*, a very rare calculus, discovered by Dr. Marcet. It has a light brown or bright brown surface; its fracture is scaly, with a brown or deep flesh colour, and becoming resinous by friction. It is distinguished by being entirely soluble in caustic potash, and precipitated by carbonic acid. It is thrown down as a white precipitate, which agglutinates in drying, and forms a pale-yellow, hard mass, which acquires a waxy lustre by friction. It is soluble in alkaline carbonates; also in nitric acid without effervescence. Its composition is expressed by $C_5N_2H_2O_2$.

2. *Cystic oxide*, a rare calculus, discovered by Dr. Wollaston. It appears, when broken, to form a yellowish-white, confused crystalline mass, having a brilliant waxy lustre. It is distinguished by its solubility in caustic potash, from which it is deposited on the addition of acetic acid, in hexagonal plates. It is also soluble in ammonia. The mineral acids dissolve cystic oxide with ease, and form crystalline compounds with it. The compound with hydrochloric acid is

anhydrous, and contains 1 atom of cystic oxide and of the acid. The nitrate contains 2 atoms of water, one of which it loses at 105° . The solution of cystic oxide in an alkali or alkaline carbonate is decomposed by heat, ammonia first coming off, and then as the evaporation proceeds, a combustible gas, which smells like sulphuret of carbon. This calculus contains sulphur, and is represented by $C_6NH_6O_4S_2$ (Thaulow).

3. *Oxalate of lime, or mulberry calculus*, has a dark-coloured tuberculated surface, is very hard and compact, rarely large. It is easily distinguished by the circumstance that its powder does not dissolve in acetic acid; but after being heated on a spatula to low redness, in the flame of a spirit-lamp, it dissolves readily in that acid with effervescence, the oxalate of lime having been converted into carbonate. The composition of crystallized oxalate of lime is $CaO, C_2O_3 + 2HO$.

4. *Bone-earth calculus*; its surface is pale brown and quite smooth, as if it had been polished. It is compact, and when sawed through, appears very regularly laminated. It is distinguished by its powder dissolving in dilute nitric and hydrochloric acid, but not in acetic acid, nor in solution of caustic potash. It appears white and not easily fused before the blow-pipe. The composition of bone-earth is expressed by $8CaO, HO + 3PO_5$.

2. *Ammoniaco-magnesian phosphate calculus* is composed of the phosphate of magnesia and ammonia, which precipitates in granular crystals when phosphoric acid is added to a mixed solution of a salt of magnesia and ammonia (page 508). It is white and less compact than the last, and sparking crystals of the salt are often perceptible in the mass. It emits ammonia when heated to 212° , is dissolved by cold acetic acid and precipitated again on neutralising the acid. It emits ammonia when digested in a solution of potash, but does not dissolve. It fuses into a white pearly globule by strong heat of the blow pipe. The composition of crystallized phosphate of magnesia and ammonia is $2MgO.NH_4O, PO_5 + 14HO$.

6. The *fusible calculus* is a mixture of the two last, is common in old and exhausted subjects, and often attains a large size. It is commonly white, rather friable and chalky; its fracture rugged and uneven, and surface dusty. It melts easily

before the blow pipe into a pearly globule. Part of it dissolves in acetic acid, the rest in hydrochloric acid.

7. The *uric acid calculus* is perhaps the most common. It is usually of an oval form, of a brownish or fawn colour and smooth surface, and composed of concentric layers round a central nucleus, which is often foreign matter. Consisting of volatile elements, like the first and second species, it is consumed before the blow pipe, leaving only a trace of white ash. The powder of this calculus is soluble in a dilute and warm solution of caustic potash, and on adding an acid, uric acid is precipitated as a white powder. It is dissolved with effervescence by nitric acid of the ordinary strength, and the solution when evaporated nearly to dryness, and treated with a drop of ammonia exhibits the beautiful pink colour of murexide (see uric acid, page 1003). The formula for uric acid is $C_{10}H_4N_4O_6$.

8. The *urate of ammonia* forms a comparatively rare calculus. It has the chemical properties of the last species, with the additional property of emitting ammonia when dissolved in a dilute and warm solution of caustic potash.

SECTION VIII.

SOLID PARTS OF ANIMALS.

Bones.—When bones are digested in very dilute hydrochloric acid, their earth is dissolved-out, and an organic matter remains, consisting of cartilage, which retains the form of the bones. This matter when moist is flexible and elastic; by drying it shrivels up and becomes brittle, but remains translucent. It is entirely dissolved by boiling in water, and gives a solution of gelatin (page 1036). Water heated above 212° , under pressure, dissolves the cartilaginous matter entirely out of bones, and leaves the pure bone-earth.

When bones are distilled in a close vessel, they yield ammonia and oily volatile products, while the earth remains behind, black, from the presence of 8 or 10 per cent of charcoal, which in this divided state and associated with the earth, has a high decolourising power. It forms animal charcoal, bone or ivory black. Bones burn white, on the other hand, in an open fire, and leave the bone-earth. The phosphate of lime in bones is

peculiar, it contains 8 proportions of lime to 3 of phosphoric acid, or $8\text{CaO} + 3\text{PO}_5$; but it is undoubtedly a compound of two tribasic phosphates of lime, namely, $2\text{CaO}, \text{HO}, \text{PO}_5 + 2(3\text{CaO}, \text{PO}_5)$; containing 1 atom of water before calcination. The proportion between the earth and cartilage varies in different bones; the human scapula has been found to contain $54\frac{1}{2}$, the temporal bone $63\frac{1}{2}$ per cent of bone-earth. Human bones well dried are said to contain 11 per cent of carbonate of lime, which is three times the quantity in the bones of the ox. Fluoride of calcium is also found in bones, although not uniformly present according to Dr. Rees' observations. The salt in question occurs in fossil bones, and is contained in considerable quantity in the human bones found in Herculaneum. In weak or ricketty bones the proportion of bone earth has been found diminished by 14 per cent. M. Valentin finds, by the analysis of morbid osseous formations, that the callus and exostosis contain more carbonate of lime than the sound bone upon which they form, and that, on the contrary, the caries contains a quantity of carbonate of lime smaller by several per cent than the sound bone.

The *teeth* are composed of the same materials as bone, but contain less cartilage; usually about 64 per cent of phosphate of lime, about 6 per cent of carbonate of lime with carbonate of magnesia, and 28 per cent of cartilage. The *ivory* of the teeth contains no cartilage, about 88 per cent of phosphate of lime, with some fluoride of calcium, and 10 per cent of carbonate of lime, with magnesia. The antlers of deer have the same composition as bone.

Skin.—The cuticle or epidermis is a coating of horny matter (page 1039), without blood-vessels. The mucous membrane (*rete Malpighi*), between the cuticle and true skin, appears to consist of the matter of the epidermis not yet hardened. The *corium* or true skin is completely decomposed by digestion in boiling water, and yields a solution of gelatin (page 1036). The composition and peculiar characters of the organic matter in *nails, claws, hoofs, hair, wool, and feathers*, have already been described (pages 1041, 1042). All these substances contain, besides, from $\frac{1}{2}$ to 2 per cent of bone-earth.

Human perspiration has an acid re-action, it is supposed from acetic acid, but from its observed effects upon the dyed colours

of prints, it must occasionally be formic acid. Its fixed constituents amount to from $\frac{1}{2}$ to $1\frac{1}{2}$ per cent, and consist of an undetermined animal matter, sal ammoniac, lactate of ammonia, chloride of sodium, and the other usual salts.

Muscle.—The threads or fibres of muscle consist essentially of fibrin (page 1024), but in addition to fibrin, several other substances are present, of which the nature is very imperfectly known. Flesh strongly dried, leaves about 23 per cent of solid matter, the other 77 per cent are water. Of the dry mass, about 6 per cent dissolves in water. Water extracts from hashed meat, about 17 per cent of its weight. This extract of meat is partly soluble in alcohol and partly insoluble. It is a mixture of salts with several organic substances, of which the true nature is still very doubtful. These undetermined extractive matters occur also in urine and most of the animal fluids. To one of them, soluble in both water and alcohol, and the cause of the odour of cooked meat, the name *osmazome* has been applied, but the matter so named has not the characters of a pure substance.

The fibrin of all animals is similar, for it has been found by Liebig, that the flesh of the ox, the deer, the cod and pike do not differ in composition.

The composition of *ligaments, cartilage, tendons, &c.* has already been described (p. 1036).

Fat.—Human fat appears to contain no stearine, but only margarine (page 959), and oleine (page 965). *Tallow*, or the melted fat of oxen and sheep, on the other hand, consists chiefly of stearine (page 961), with a little oleine. It forms excellent hard *soaps*; in the preparation of which, the melted tallow is boiled with a solution of caustic soda, weak at first, but gradually increased in strength; the soap floats upon the alkaline liquor, in which it is insoluble, while the glycerine of the tallow, which has been replaced in combination with the stearic and oleic acids, by soda, is dissolved by the water. In the formation of the common *diachylon plaster*, 9 parts of olive oil and some water are boiled with 5 parts of levigated litharge; a compound of margaric and oleic acids with the oxide of lead results, which forms a plastic mass, and is an insoluble soap. *Hog's lard* contains more oleine than tallow, and is softer; it probably, like human fat, contains margarine, although stearine also is undoubtedly present.

Brain and nerves.—The substance of the brain has been examined by more than one chemist, but most recently by M. Fremy. The brain of man contains 7 parts of albumen, 5 parts of a fatty matter, and 80 parts of water. The albuminous portion, after being coagulated by heat, is insoluble in water, alcohol and ether. The fatty matter is what has principally occupied attention; besides portions of the ordinary fatty substances, it contains two peculiar acids and cholesterin:

1. *Cerebric acid* which when purified is white, and presents itself in crystalline grains. It dissolves without residue in boiling alcohol, is almost insoluble in cold ether, more soluble in boiling ether. It has the remarkable property of swelling up like starch in boiling water, but appears to be insoluble in that liquid. It enters into fusion at a high temperature, approaching closely that at which it is decomposed, and is combustible. It contains no sulphur, but some phosphorus. The result of its analysis by Fremy, is 66.7 per cent of carbon, 10.6 of hydrogen, 2.3 of nitrogen, 0.9 of phosphorus, 19.5 of oxygen.

2. *Oleophosphoric acid*, which is separated from the former acid, by its solubility in ether. It is still accompanied by oleine and cholesterin, which are withdrawn from it by alcohol and ether. This acid is of a viscid consistence, insoluble in cold alcohol, but dissolving easily in boiling alcohol; it is insoluble in ether. Placed in contact with potash, soda and ammonia, it immediately gives soapy compounds. It forms compounds insoluble in water with other bases. M. Fremy has observed a remarkable transformation of oleophosphoric acid. When boiled for a long time in water or alcohol, it gradually loses its viscosity and becomes a fluid oil, which is pure *oleine*; while the liquor contains phosphoric acid. This decomposition becomes very rapid, when the liquor is rendered slightly acid. Although M. Fremy's attempts to form this acid directly, by uniting oleine and phosphoric acid, were unsuccessful, he still deems it probable that this acid may consist of the elements in question, and be analogous to the compound of sulphuric acid and oleine or sulpholeic acid (page 968). It contains from 1.9 to 2 per cent of phosphorus, in the condition, it is thus represented, of phosphoric acid.

M. Fremy has given a process for extracting cholesterin (page 1048) from the brain, in considerable quantity.

The constituents of the brain of man, enumerated by Fremy, are : 1. Cerebric acid free or combined with soda, or with phosphate of lime. 2. Oleophosphoric acid free and combined with soda. 3. Oleine and margarine. 4. Minute quantities of oleic and margaric acids. 5. Cholesterin. 6. Water and an albuminous matter. These results are quite different from those previously obtained by M. Couerbe, whose method of investigation appears to have been defective.

Fremy found a considerable quantity of cerebral matter in the spinal marrow, and very appreciable quantities of it in certain nerves.

The eye.—The *sclerotica* is dissolved, like the corium, by long boiling with water, and gives a solution of gelatin; it is said to contain no fibrin. The *cornea* is composed of cartilaginous fibres, and therefore consists of chondrin; but it contains besides, a small quantity of fibrin or albumen. The *pigmentum nigrum* (page 1043) has considerable resemblance to hematosin. The *vitreous* and *aqueous humours* consist of water with about $1\frac{1}{2}$ per cent of common salt, a little albumen and undetermined animal matter. The substance of the *crystalline lens* agrees in properties with the globulin of the blood, and may be represented as a compound of 15 atoms of protein with 1 atom of sulphur. When rubbed in pure water, the greater part of the crystalline dissolves; the solution is coagulated by heat, and forms a granular and not a coherent mass. The crystalline undergoes the same coagulation when put into hot water, into alcohol, or into an acid.

APPENDIX.

TABLE I.

For the conversion of degrees on the Centigrade thermometer into degrees of Fahrenheit's scale.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—50 ⁰	—58 ⁰ .0	— 9 ⁰	15 ⁰ .8	32 ⁰	89 ⁰ .6
—49	—56.2	— 8	17.6	33	91.4
—48	—54.4	— 7	19.4	34	93.2
—47	—52.6	— 6	21.2	35	95.0
—46	—50.8	— 5	23.0	36	96.8
—45	—49.0	— 4	24.8	37	98.6
—44	—47.2	— 3	26.6	38	100.4
—43	—45.4	— 2	28.4	39	102.2
—42	—43.6	— 1	30.2	40	104.0
—41	—41.8	0	32.0	41	105.8
—40	—40.0	+ 1	33.8	42	107.6
—39	—38.2	2	35.6	43	109.4
—38	—36.4	3	37.4	44	111.2
—37	—34.6	4	39.2	45	113.0
—36	—32.8	5	41.0	46	114.8
—35	—30.0	6	42.8	47	116.6
—34	—29.2	7	44.6	48	118.4
—33	—27.4	8	46.4	49	120.2
—32	—25.6	9	48.2	50	122.0
—31	—23.8	10	50.0	51	123.8
—30	—22.0	11	51.8	52	125.6
—29	—20.2	12	53.6	53	127.4
—28	—18.4	13	55.4	54	129.2
—27	—16.6	14	57.2	55	131.0
—26	—14.8	15	59.0	56	132.8
—25	—13.0	16	60.8	57	134.6
—24	—11.2	17	62.6	58	136.4
—23	— 9.4	18	64.4	59	138.2
—22	— 7.6	19	66.2	60	140.0
—21	— 5.8	20	68.0	61	141.8
—20	— 4.0	21	69.8	62	143.6
—19	— 2.2	22	71.6	63	145.4
—18	— 0.4	23	73.4	64	147.2
—17	+ 1.4	24	75.2	65	149.0
—16	3.2	25	77.0	66	150.8
—15	5.0	26	78.8	67	152.6
—14	6.8	27	80.6	68	154.4
—13	8.6	28	82.4	69	156.2
—12	10.4	29	84.2	70	158.0
—11	12.2	30	86.0	71	159.8
—10	14.0	31	87.8	72	161.6

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
73 ⁰	163 ⁰ .4	121 ⁰	249 ⁰ .8	169 ⁰	336 ⁰ .2
74	165 .2	122	251 .6	170	338 .0
75	167 .0	123	253 .4	171	339 .8
76	168 .8	124	255 .2	172	341 .6
77	170 .6	125	257 .0	173	343 .4
78	172 .4	126	258 .8	174	345 .2
79	174 .2	127	260 .6	175	347 .0
80	176 .0	128	262 .4	176	348 .8
81	177 .8	129	264 .2	177	350 .6
82	179 .6	130	266 .0	178	352 .4
83	181 .4	131	267 .8	179	354 .2
84	183 .2	132	269 .6	180	356 .0
85	185 .0	133	271 .4	181	357 .8
86	186 .8	134	273 .2	182	359 .6
87	188 .6	135	275 .0	183	361 .4
88	190 .4	136	276 .8	184	363 .2
89	192 .2	137	278 .6	185	365 .0
90	194 .0	138	280 .4	186	366 .8
91	195 .8	139	282 .2	187	368 .6
92	197 .6	140	284 .0	188	370 .4
93	199 .4	141	285 .8	189	372 .2
94	201 .2	142	287 .6	190	374 .0
95	203 .0	143	289 .4	191	375 .8
96	204 .8	144	291 .2	192	377 .6
97	206 .6	145	293 .0	193	379 .4
98	208 .4	146	294 .8	194	381 .2
99	210 .2	147	296 .6	195	383 .0
100	212 .0	148	298 .4	196	384 .8
101	213 .8	149	300 .2	197	386 .6
102	215 .6	150	302 .0	198	388 .4
103	217 .4	151	303 .8	199	390 .2
104	219 .2	152	305 .6	200	392 .0
105	221 .0	153	307 .4	201	393 .8
106	222 .8	154	309 .2	202	395 .6
107	224 .6	155	311 .0	203	397 .4
108	226 .4	156	312 .8	204	399 .2
109	228 .2	157	314 .6	205	401 .0
110	230 .0	158	316 .4	206	402 .8
111	231 .8	159	318 .2	207	404 .6
112	233 .6	160	320 .0	208	406 .4
113	235 .4	161	321 .8	209	408 .2
114	237 .2	162	323 .6	210	410 .0
115	239 .0	163	325 .4	211	411 .8
116	240 .8	164	327 .2	212	413 .6
117	242 .6	165	329 .0	213	415 .4
118	244 .4	166	330 .8	214	417 .2
119	246 .2	167	332 .6	215	419 .0
120	248 .0	168	334 .4	216	420 .8

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
217 ⁰	422 ⁰ .6	252 ⁰	485 ⁰ .6	287 ⁰	548 ⁰ .6
218	424.4	253	487.4	288	550.4
219	426.2	254	489.2	289	552.2
220	428.0	255	491.0	290	554.0
221	429.8	256	492.8	291	555.8
222	431.6	257	494.6	292	557.6
223	433.4	258	496.4	293	559.4
224	435.2	259	498.2	294	561.2
225	437.0	260	500.0	295	563.0
226	438.8	261	501.8	296	564.8
227	440.6	262	503.6	297	566.6
228	442.4	263	505.4	298	568.4
229	444.2	264	507.2	299	570.2
230	446.0	265	509.0	300	572.0
231	447.8	266	510.8	301	573.8
232	449.6	267	512.6	302	575.6
233	451.4	268	514.4	303	577.4
234	453.2	269	516.2	304	579.2
235	455.0	270	518.0	305	581.0
236	456.8	271	519.8	306	582.8
237	458.6	272	521.6	307	584.6
238	460.4	273	523.4	308	586.4
239	462.2	274	525.2	309	588.2
240	464.0	275	527.0	310	590.0
241	465.8	276	528.8	311	591.8
242	467.6	277	530.6	312	593.6
243	469.4	278	532.4	313	595.4
244	471.2	279	534.2	314	597.2
245	473.0	280	536.0	315	599.0
246	474.8	281	537.8	316	600.8
247	476.6	282	539.6	317	602.6
248	478.4	283	541.4	318	604.4
249	480.2	284	543.2	319	606.2
250	482.0	285	545.0	320	608.0
251	483.8	286	546.8		

TABLE II.

TABLE of the elastic Force of Aqueous Vapour at different Temperatures, expressed in Inches of Mercury.

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
32° F.	0.200	0.200	80° F.	1.00	1.010	128° F.	4.11	
33	0.207		81	1.04		129	4.22	
34	0.214		82	1.07		130	4.34	4.366
35	0.221		83	1.10		131	4.47	
36	0.229		84	1.14		132	4.60	
37	0.237		85	1.17	1.170	133	4.73	
38	0.245		86	1.21		134	4.86	
39	0.254		87	1.24		135	5.00	5.070
40	0.263	0.250	88	1.28		136	5.14	
41	0.273		89	1.32		137	5.29	
42	0.283		90	1.36	1.360	138	5.44	
43	0.294		91	1.40		139	5.59	
44	0.305		92	1.44		140	5.74	5.770
45	0.316		93	1.48		141	5.90	
46	0.328		94	1.53		142	6.05	
47	0.339		95	1.58	1.640	143	6.21	
48	0.351		96	1.63		144	6.37	
49	0.363		97	1.68		145	6.53	6.600
50	0.375	0.360	98	1.74		146	6.70	
51	0.388		99	1.80		147	6.87	
52	0.401		100	1.86	1.860	148	7.05	
53	0.415		101	1.92		149	7.23	
54	0.429		102	1.98		150	7.42	7.530
55	0.443	0.416	103	2.04		151	7.61	
56	0.458		104	2.11		152	7.81	
57	0.474		105	2.18	2.100	153	8.01	
58	0.490		106	2.25		154	8.20	
59	0.507		107	2.32		155	8.40	8.500
60	0.524	0.516	108	2.39		156	8.60	
61	0.542		109	2.46		157	8.81	
62	0.560		110	2.53	2.456	158	9.02	
63	0.578		111	2.60		159	9.24	
64	0.597		112	2.68		160	9.46	9.600
65	0.616	0.630	113	2.76		161	9.68	
66	0.635		114	2.84		162	9.91	
67	0.655		115	2.92	2.820	163	10.15	
68	0.676		116	3.00		164	10.41	
69	0.698		117	3.08		165	10.68	10.800
70	0.721	0.726	118	3.16		166	10.96	
71	0.745		119	3.25		167	11.25	
72	0.770		120	3.33	2.300	168	11.54	
73	0.796		121	3.42		169	11.83	
74	0.823		122	3.50		170	12.13	12.050
75	0.851	0.860	123	3.59		171	12.43	
76	0.880		124	3.69		172	12.73	
77	0.910		125	3.79	3.830	173	13.02	
78	0.940		126	3.89		174	13.32	
79	0.971		127	4.00		175	13.62	13.550

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure		Dalton.	Ure.
176° F.	13.92		201° F.	24.12		226° F.	38.89	40.100
177	14.22		202	24.61		227	39.59	
178	14.52		203	25.10		228	40.30	
179	14.83		204	25.61		229	41.02	
180	15.15	15.160	205	26.13	25.900	230	41.75	43.100
181	15.50		206	26.66		231	42.49	
182	15.86		207	27.20		232	43.24	
183	16.23		208	27.74		233	44.00	
184	16.61		209	28.29		234	44.78	46.800
185	17.00	16.900	210	28.84	28.880	235	45.58	47.220
186	17.40		211	29.41		236	46.39	
187	17.80		212	30.00	30.000	237	47.20	
188	18.20		213	30.60		238	48.02	50.300
189	18.60		214	31.21		239	48.84	
190	19.00	19.000	215	31.83		240	49.67	51.700
191	19.42		216	32.46	33.400	241	50.50	
192	19.86		217	33.09		242	51.34	53.600
193	20.32		218	33.72		243	52.18	
194	20.77		219	34.35		244	53.03	
195	21.22	21.100	220	34.99	35.540	245	53.88	56.340
196	21.68		221	35.63	36.700	246	54.68	
197	22.13		222	36.25		247	55.54	
198	22.69		223	36.88		248	56.42	60.400
199	23.16		224	37.53		249	57.31	
200	23.64	23.600	225	38.20	39.110	250	58.21	61.900

TABLE III.

Dr. Ure's Table of the Quantity of Oil of Vitriol, of sp. gr. 1.8485, and of Anhydrous Acid, in 100 Parts of dilute Sulphuric Acid, at different Densities.

Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.
100	1.8485	81.54	66	1.5503	53.82	32	1.2334	26.09
99	1.8475	80.72	65	1.5390	53.00	31	1.2260	25.23
98	1.8460	79.90	64	1.5280	52.18	30	1.2184	24.46
97	1.8439	79.09	63	1.5170	51.37	29	1.2108	23.65
96	1.8410	78.28	62	1.5066	50.55	28	1.2032	22.83
95	1.8376	77.46	61	1.4960	49.74	27	1.1956	22.01
94	1.8336	76.65	60	1.4860	48.92	26	1.1876	21.20
93	1.8290	75.83	59	1.4760	48.11	25	1.1792	20.38
92	1.8233	75.02	58	1.4660	47.29	24	1.1706	19.57
91	1.8179	74.20	57	1.4560	46.48	23	1.1626	18.75
90	1.8115	73.39	56	1.4460	45.66	22	1.1549	17.94
89	1.8043	72.57	55	1.4360	44.85	21	1.1480	17.12
88	1.7962	71.75	54	1.4265	44.03	20	1.1410	16.31
87	1.7870	70.94	53	1.4170	43.22	19	1.1330	15.49
86	1.7774	70.12	52	1.4073	42.40	18	1.1246	14.68
85	1.7673	69.31	51	1.3977	41.58	17	1.1165	13.86
84	1.7570	68.49	50	1.3884	40.77	16	1.1090	13.05
83	1.7465	67.68	49	1.3788	39.95	15	1.1019	12.23
82	1.7360	66.86	48	1.3697	39.14	14	1.0953	11.41
81	1.7245	66.05	47	1.3612	38.32	13	1.0887	10.60
80	1.7126	65.23	46	1.3530	37.51	12	1.0809	9.78
79	1.6993	64.42	45	1.3440	36.69	11	1.0743	8.97
78	1.6870	63.60	44	1.3345	35.88	10	1.0682	8.15
77	1.6750	62.78	43	1.3255	35.06	9	1.0614	7.34
76	1.6630	61.97	42	1.3165	34.25	8	1.0544	6.52
75	1.6520	61.15	41	1.3080	33.43	7	1.0477	5.71
74	1.6415	60.34	40	1.2999	32.61	6	1.0405	4.89
73	1.6321	59.52	39	1.2913	31.80	5	1.0336	4.08
72	1.6204	58.71	38	1.2826	30.98	4	1.0268	3.26
71	1.6090	57.89	37	1.2740	30.17	3	1.0206	2.446
70	1.5975	57.08	36	1.2654	29.35	2	1.0140	1.63
69	1.5868	56.26	35	1.2572	28.54	1	1.0074	0.8154
68	1.5760	55.45	34	1.2490	27.72			
67	1.5648	54.63	33	1.2409	26.91			

TABLE IV.

Dr. Ure's Table of the Quantity of Real or Anhydrous Nitric Acid in 100 Parts of Liquid Acid at different Densities.

Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.
1.5000	79.700	1.3783	52.602	1.1895	26.301
1.4980	78.903	1.3732	51.805	1.1833	25.504
1.4960	78.106	1.3681	51.068	1.1770	24.707
1.4940	77.309	1.3630	50.211	1.1709	23.910
1.4910	76.512	1.3579	49.414	1.1648	23.113
1.4880	75.715	1.3529	48.617	1.1587	22.316
1.4850	74.918	1.3477	47.820	1.1526	21.519
1.4820	74.121	1.3427	47.023	1.1465	20.722
1.4790	73.324	1.3376	46.226	1.1403	19.925
1.4760	72.527	1.3323	45.429	1.1345	19.128
1.4730	71.730	1.3270	44.632	1.1286	18.331
1.4700	70.933	1.3216	43.835	1.1227	17.534
1.4670	70.136	1.3163	43.038	1.1168	16.737
1.4640	69.339	1.3110	42.241	1.1109	15.940
1.4600	68.542	1.3056	41.444	1.1051	15.143
1.4570	67.745	1.3001	40.647	1.0993	14.346
1.4530	66.948	1.2947	39.850	1.0935	13.549
1.4500	66.155	1.2887	39.053	1.0878	12.752
1.4460	65.354	1.2826	38.256	1.0821	11.955
1.4424	64.557	1.2765	37.459	1.0764	11.158
1.4385	63.760	1.2705	36.662	1.0708	10.361
1.4346	62.963	1.2644	35.865	1.0651	9.564
1.4306	62.166	1.2583	35.068	1.0595	8.767
1.4269	61.369	1.2523	34.271	1.0540	7.970
1.4228	60.572	1.2462	33.474	1.0485	7.173
1.4189	59.775	1.2402	32.677	1.0430	6.376
1.4147	58.978	1.2341	31.880	1.0375	5.579
1.4107	58.181	1.2277	31.083	1.0320	4.782
1.4065	57.384	1.2212	30.286	1.0267	3.985
1.4023	56.587	1.2148	29.489	1.0212	3.188
1.3978	55.790	1.2084	28.692	1.0159	2.391
1.3945	54.993	1.2019	27.895	1.0106	1.594
1.3882	54.196	1.1958	27.098	1.0053	0.797
1.3833	53.399				

TABLE V.

Table of M. Lowitz, showing the Quantity of absolute Alcohol in Spirits of different Specific Gravities.

100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.	
Alc.	Wat.	At 60°.	At 68°.	Alc.	Wat.	At 60°.	At 68°.	Alc.	Wat.	At 60°.	At 68°.
100	0	0.796	0.791	66	34	0.881	0.877	32	68	0.955	0.952
99	1	0.798	0.794	65	35	0.883	0.880	31	69	0.957	0.954
98	2	0.801	0.797	64	36	0.886	0.882	30	70	0.958	0.956
97	3	0.804	0.800	63	37	0.889	0.885	29	71	0.960	0.957
96	4	0.807	0.803	62	38	0.891	0.887	28	72	0.962	0.959
95	5	0.809	0.805	61	39	0.893	0.889	27	73	0.963	0.961
94	6	0.812	0.808	60	40	0.896	0.892	26	74	0.965	0.963
93	7	0.815	0.811	59	41	0.898	0.894	25	75	0.967	0.965
92	8	0.817	0.813	58	42	0.900	0.896	24	76	0.968	0.966
91	9	0.820	0.816	57	43	0.902	0.899	23	77	0.970	0.968
90	10	0.822	0.818	56	44	0.905	0.901	22	78	0.972	0.970
89	11	0.825	0.821	55	45	0.906	0.903	21	79	0.973	0.971
88	12	0.827	0.823	54	46	0.908	0.905	20	80	0.974	0.973
87	13	0.830	0.826	53	47	0.910	0.907	19	81	0.975	0.974
86	14	0.832	0.828	52	48	0.912	0.909	18	82	0.977	0.976
85	15	0.835	0.831	51	49	0.915	0.912	17	83	0.978	0.977
84	16	0.838	0.834	50	50	0.917	0.914	16	84	0.979	0.978
83	17	0.840	0.836	49	51	0.920	0.917	15	85	0.981	0.980
82	18	0.843	0.839	48	52	0.922	0.919	14	86	0.982	0.981
81	19	0.846	0.842	47	53	0.924	0.921	13	87	0.984	0.983
80	20	0.848	0.844	46	54	0.926	0.923	12	88	0.986	0.985
79	21	0.851	0.847	45	55	0.928	0.925	11	89	0.987	0.986
78	22	0.853	0.849	44	56	0.930	0.927	10	90	0.988	0.987
77	23	0.855	0.851	43	57	0.933	0.930	9	91	0.989	0.988
76	24	0.857	0.853	42	58	0.935	0.932	8	92	0.990	0.989
75	25	0.860	0.856	41	59	0.937	0.934	7	93	0.992	0.991
74	2	0.863	0.859	40	60	0.939	0.936	6	94	0.991	0.992
73	27	0.865	0.861	39	61	0.941	0.938	5	95		0.994
72	28	0.867	0.863	38	62	0.943	0.940	4	96		0.995
71	29	0.870	0.866	37	63	0.945	0.942	3	97		0.997
70	30	0.872	0.868	36	64	0.947	0.944	2	98		0.998
69	31	0.874	0.870	35	65	0.949	0.946	1	99		0.999
68	32	0.875	0.872	34	66	0.951	0.948	0	100		1.000
67	33	0.879	0.875	33	67	0.953	0.950				

TABLE VI.

Tables showing the Specific Gravity of Liquids, at the Temperature of 55° Fahr. corresponding to the Degrees of Beaumé's Hydrometer.

For Liquids lighter than Water.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
10	1.000	17	.949	23	.874	29	.807	35	.742
11	.990	18	.942	24	.867	30	.797	36	.732
12	.985	19	.935	25	.861	31	.789	37	.727
13	.977	20	.928	26	.856	32	.783	38	.722
14	.970	21	.922	27	.852	33	.779	39	.720
15	.963	22	.915	28	.847	34	.774	40	.717
16	.955								

For Liquids heavier than Water.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
0	1.000	15	1.114	30	1.261	45	1.455	60	1.717
3	1.020	18	1.140	33	1.295	48	1.500	63	1.779
6	1.040	21	1.170	36	1.333	51	1.547	66	1.848
9	1.064	24	1.200	39	1.373	54	1.594	69	1.920
12	1.089	27	1.230	42	1.414	57	1.639	72	2.000

TABLE VII.

TABLES FOR REFERENCE IN QUALITATIVE ANALYSIS.

I. GASES.

Distinctive properties of oxygen, nitrogen, protoxide of nitrogen, deutoxide of nitrogen, hydrogen, carbonic oxide and carbonic acid.

GASES.		
Soluble in water.	{ Carbonic acid Protoxide of nitrogen }	Solution disturbs lime-water. Does not.
Support combustion	{ Oxygen Protoxide of nitrogen }	
Combustible	{ Carbonic oxide Hydrogen }	Product of combustion disturbs lime-water. Does not.
Extinguish combustion	{ Deutoxide of nitrogen Nitrogen }	Forms brown fumes with oxygen. Does not.

II. ACIDS.

Distinctive properties of certain acids, in combination.

ACIDS.		
Precipitated by chloride of barium	Sulphuric	{ Precipitate not dissolved by nitric acid.
	Iodic	
	Sulphurous	{ Precipitate dissolved by hydrochloric acid.
	Phosphoric	
	Pyrophosphoric	
	Carbonic	
Precipitated by nitrate of silver	Hyposulphurous	{ Precipitate not dissolved by nitric acid.
	Hydrochloric, white	
	Hydriodic, yellow	{ Precipitate dissolved by nitric acid.
	Phosphoric	
	Pyrophosphoric	
	Iodic	
	Carbonic	{ „ sulphur appears.
	Sulphurous	
	Hyposulphurous	

ACIDS.

Indicated by strong sul- phuric acid.	{	Carbonic	{	Effervescence of a gas which renders lime-water turbid.
		Sulphurous		Effervescence : gas decom- poses iodic acid.
		Hyposulphurous		Effervescence of sulphurous acid, and sulphur deposit- ed.
		Hydriodic		Iodine liberated.
		Chloric		Peroxide of chlorine evolved, and liquid bleaches.

SPECIAL TESTS.

Hydriodic acid, by chlorine-water and starch.

Iodic acid, by sulphurous acid water and starch.

Sulphurous acid, by iodic acid and starch.

Nitric acid, by sulphate of indigo.

Hyposulphurous acid dissolves chloride of silver.

„ „ is *not* precipitated by nitrate of strontian.

III. ALKALIES AND EARTHS.

Distinctive properties of potash, soda, ammonia, barytes, lime, strontian, magnesia and alumina, in their salts ; the re-agents to be applied in succession as numbered.

RE-AGENTS.

1 ^o Carbonate of soda	Precipitates earths and not alkalies.
2 ^o Oxalate of ammonia	Precipitates barytes, strontian and lime.
3 ^o Diluted sulphate of soda	{ Precipitates barytes and strontian, but not lime.
4 ^o Hyposulphite of soda	
	Precipitates barytes but not strontian.

SPECIAL TESTS.

Caustic potash evolves *ammonia*.

Tartaric acid in excess precipitates *potash*.

Bicarbonate of potash does not precipitate *magnesia*.

Caustic potash dissolves *alumina*.

IV. METALLIC OXIDES.

Distinctive properties of the oxides of certain of the metals proper, in their salts.

METALLIC OXIDES.	RE-AGENTS.			SPECIAL TESTS.
	Caustic potash.	Sulphuretted hydrogen ; the metallic solutions be- ing made strongly acid by a mineral acid.	Hydrosulphuret of am- monium.	
Protox. manganese	white, becoming brown	.	flesh-colour	{ Chloride of lime gives manganese brown.
Protox. iron	white, becoming green	.	black	{ Red prussiate of potash gives Prussian blue.
Perox. iron	ochry red	a little sulphur	black	{ Yellow prussiate of potash gives Prussian blue.
Oxide of zinc	white	.	white	{ Ammonia re-dissolves oxide.
Oxide of copper	blue	black	brown black	{ Ammonia forms a deep blue solution.
Oxide of lead	white soluble in excess	black	black	{ Iodide of potassium gives yellow iodide.
Protoxide of tin	{ white, may dissolve in excess	brown black	brown black	{ Chloride of mercury, white and black.
Peroxide of tin	{ white, may dissolve in excess	light yellow	light yellow	{ Ignited oxide is not soluble in acids.
Oxide of chromium	dull green	.	dull green oxide sulphur and oxide of chromium	{ Ditto.
Chromic acid	.	{ sulphur and oxide of chromium		{ Acetate of lead gives a yellow precipitate.

TABLE VIII.

SELECTED ATOMIC WEIGHTS, WITH THEIR LOGARITHMS, FOR THE
CALCULATIONS OF ANALYSIS.

The numbers are the same as those given in the body of the work (from Berzelius), with the exception of carbon, which is always taken here at 75, (Dumas), and nitrogen at 175.6; the last deduced by Dr. Clark from M. Dumas' recent determinations of the densities of nitrogen and oxygen.

Name.	Symbol.	Atomic Weight.	Logarithm.
Ammonia . . .	NH ₃	213.13	2.32864
Antimony . . .	Sb	1612.9	3.20761
— (oxide of) . .	SbO ₃	1912.9	3.28169
— (sulphuret of) .	SbS ₃	2216.4	3.34565
Arsenic . . .	As	940.1	2.973174
— (sulphuret of) .	AsS ₃	1543.6	3.18854
— (sulphuret of) .	AsS ₅	1945.9	3.28912
Arsenic acid . .	AsO ₅	1440.1	3.15839
Arsenious acid . .	AsO ₃	1240.1	3.09346
Barium . . .	Ba	856.88	2.93292
— (chloride of) .	BaCl	1299.5	3.11378
Barytes . . .	BaO	956.88	2.98086
— (carbonate of) .	BaO, CO ₂	1231.9	3.09058
— (phosphate of) .	2BaO, PO ₅	2806.1	3.44811
— (sulphate of) .	BaO, SO ₃	1458.1	3.16379
Calcium, chloride of .	CaCl	698.67	2.84427
Carbon . . .	C	75.00	1.87506
Carbonic acid . .	CO ₂	275.00	2.43933
Carbonic oxide . .	CO	175.00	2.24304
Copper . . .	Cu	395.70	2.59737
— (protoxide of) .	CuO	495.70	2.69522
— (suboxide of) .	Cu ₂ O	891.39	2.95007
Hydrogen . . .	H	12.48	1.09621
Iron . . .	Fe	339.21	2.53047
— (peroxide of) .	Fe ₂ O ₃	978.43	2.99053
— (protoxide of) .	FeO	439.21	2.64267
Lead . . .	Pb	1294.5	3.11210
— (carbonate of) .	PbO, CO ₂	1669.5	3.22259
— (chloride of) .	PbCl	1737.1	3.23983
— (phosphate of) .	2PbO, PO ₅	3681.3	3.56600
— (protoxide of) .	PbO	1394.5	3.14442
— (sulphate of) .	PbO, SO ₃	1895.7	3.27777
Lime . . .	CaO	356.02	2.55147
— (carbonate of) .	CaO, CO ₂	631.03	2.80004
— (sulphate of) .	CaO, SO ₃	857.19	2.93308
Magnesia . . .	MgO	258.35	2.41220
— (sulphate of) .	MgO, SO ₃	759.52	2.88054
Manganese . . .	Mn	345.90	2.53895
— (protoxide of) .	MnO ₃	445.90	2.64924
— (deutoxide of) .	Mn ₂ O ₃	991.80	2.99642
Mercury . . .	Hg	1265.8	3.10236
— (subchloride of) .	$\frac{1}{2}$ (Hg ₂ Cl)	1487.1	3.17234
— (oxide of) .	HgO	1365.8	3.13539
— (suboxide of) .	Hg ₂ O	2631.6	3.42022

Name.	Symbol.	Atomic Weight.	Logarithm.
Nitrogen	N	175.6	2.24452
Phosphoric acid . .	PO ₅	892.31	2.95052
Phosphorous acid . .	PO ₃	692.21	2.84030
Phosphorus	P	392.31	2.59363
Platinum	Pt	1233.3	3.09107
— (ammonium chlo- ride of)	{ Pt, Cl ₂ + NH ₄ Cl }	2786.5	3.44506
— (potassium chlo- ride of)	PtCl ₂ + KCl	3051.2	3.48447
Potash	KO	589.92	2.77079
— (carbonate of) . .	KO, CO ₂	864.93	2.93698
— (sulphate of) . .	KO, SO ₃	1091.1	3.03786
Potassium	K	489.92	2.69013
— (chloride of) . .	KCl	932.57	2.96968
Silver	Ag	1351.6	3.13085
— (chloride of) . .	AgCl	1794.3	3.25389
— (oxide of) . . .	AgO	1451.6	3.16185
	—2	2903.2	3.46288
	—3	4354.8	3.63897
	—4	5806.4	3.76391
	—5	7258.0	3.86082
Soda	NaO	390.90	2.59207
— (carbonate of) . .	NaO, CO ₂	665.91	2.82341
— (sulphate of) . .	NaO, SO ₃	892.07	2.95040
Sodium	Na	290.90	2.46374
— (chloride of) . .	NaCl	733.55	2.86543
Strontian	SrO	647.29	2.81110
— (carbonate of) . .	SrO, CO ₂	922.30	2.96487
— (sulphate of) . .	SrO, SO ₃	1148.50	3.06013
Strontium, chloride of .	SrCl	989.94	2.99561
Sulphur	S	201.17	2.30356
Sulphuric acid . . .	SO ₃	501.17	2.69998
Sulphurous acid . . .	SO ₂	401.17	2.60333
Tin	Sn	735.29	2.86645
— (peroxide of) . .	SnO ₂	935.29	2.97095
— (protoxide of) . .	SnO	835.29	2.92184
Water	HO,	112.48	2.05107
	2	224.96	2.35210
	3	337.44	2.52820
	4	449.92	2.65314
	5	562.40	2.75005
	6	674.88	2.82923
	7	787.36	2.89618
	8	899.84	2.95417
	9	1012.3	3.00531
	10	1124.8	3.05107
	11	1237.3	3.09248
	12	1349.8	3.13027
	13	1462.2	3.16501
Zinc	Zn	403.23	2.60555
— (oxide of) . . .	ZnO 1	503.23	2.70177
	2	1006.5	3.00281
	3	1509.7	3.17889
	4	2012.9	3.30382

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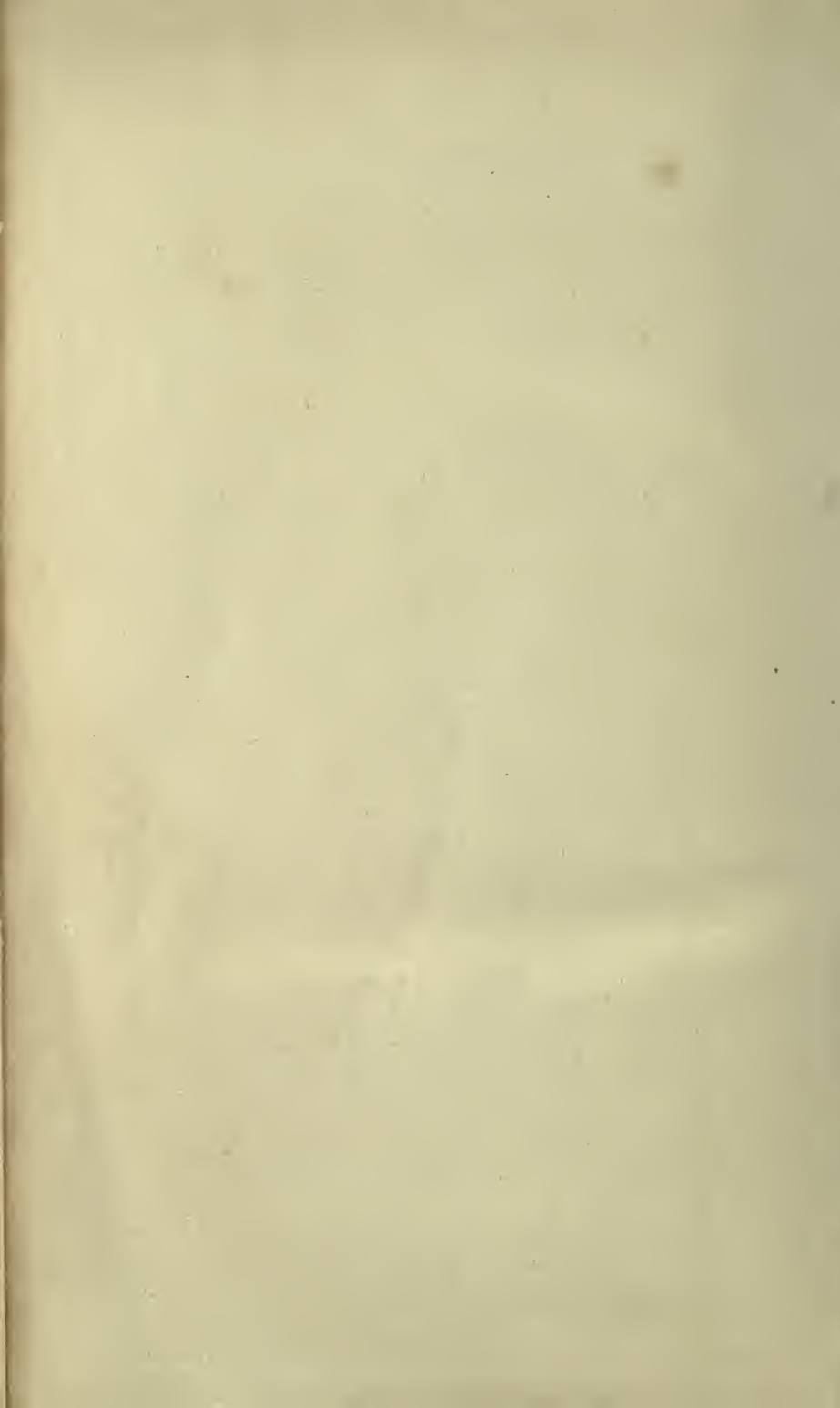
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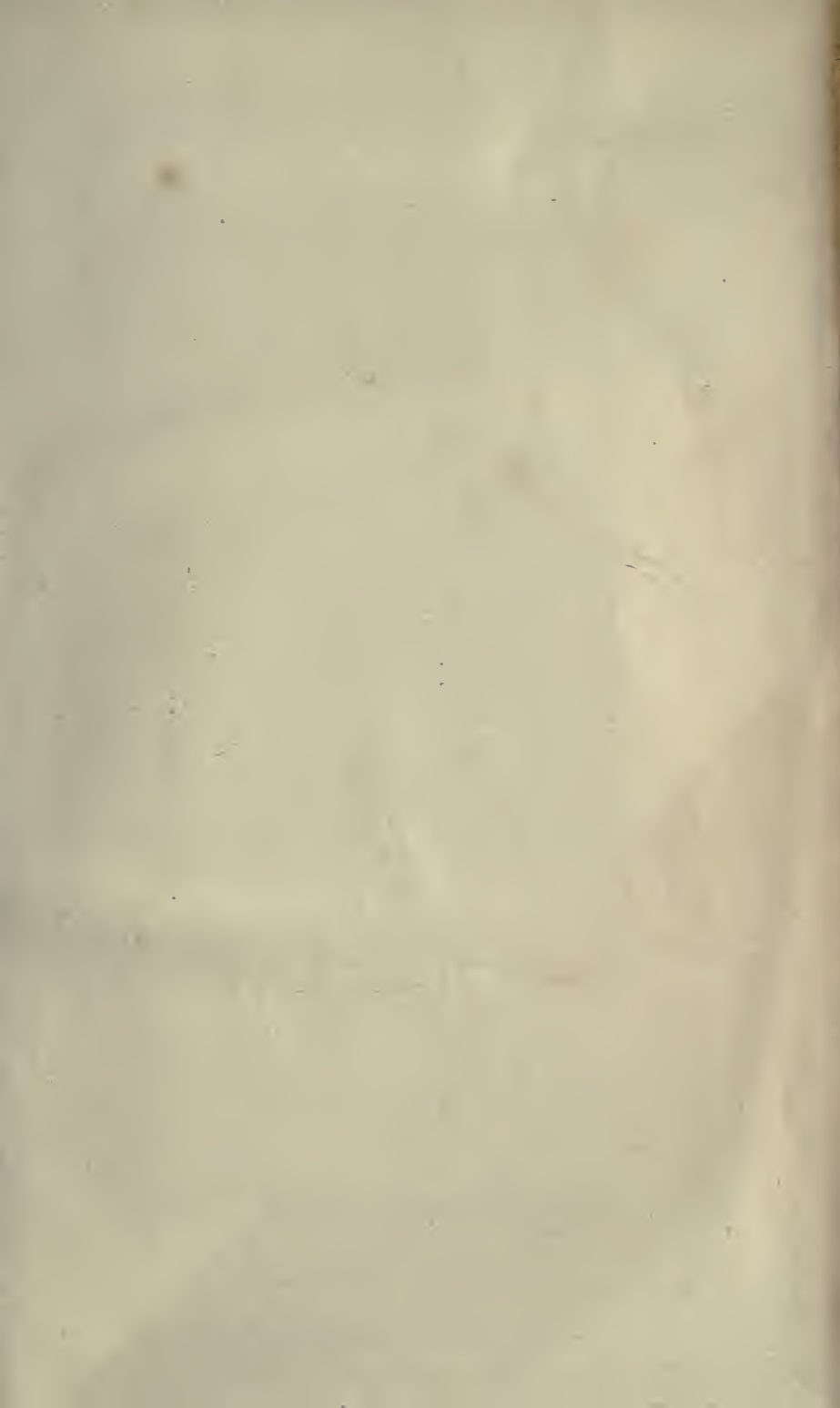
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